

**OXIDATION STATES OF CHROMIUM-51 IN SOLUTIONS OF
THERMAL-NEUTRON-IRRADIATED CHROMATES AND DICHROMATES**

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In Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

By

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to the

**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

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DEDICATED
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my beloved parents.

STATEMENT

I hereby declare that the matter embodied in this thesis is the results of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor Shankar Mukherji.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Kanpur

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September, 1988.

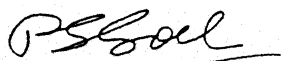
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Chm 534	Electronics for Chemistry
Chm 543	Introduction to Nuclear Chemistry
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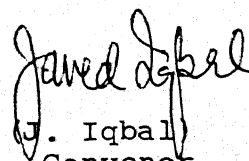
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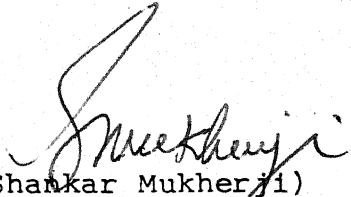
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Certified that the work contained in this thesis entitled, "OXIDATION STATES OF CHROMIUM-51 IN SOLUTIONS OF THERMAL NEUTRON IRRADIATED CHROMATES AND DICHROMATES" has been carried out by Ms. Chandra Bhattacharjee under my supervision and has not been submitted elsewhere for a degree.

Kanpur

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SYNOPSIS

The thesis entitled "Oxidation States of Chromium-51 in Solutions of Thermal-Neutron-Irradiated Chromates and Dichromates" has been divided into five chapters.

Chapter I presents an overview of the earlier work carried out using neutron-irradiated organic and inorganic systems and outlines the scope of the present work.

Chapter II describes the experimental procedure and has been subdivided into five sections. Section 2.1 summarizes the different analytical procedures used earlier for the separation of the various ^{51}Cr -species present in solutions of thermal-neutron-irradiated (TNI) chromates and dichromates. It also describes the special advantage in using short-column ion exchange chromatography in studies of this type. Further this section outlines the planning and the sequence of the present experiments. Section 2.2 outlines the general principles of ion exchange chromatography and the types of ion exchange resins used in the present experiments. Section 2.3 describes the experimental procedure in detail including the irradiation of the samples and the calibration of the columns. For anion exchange column, chemical precipitation and spectrophotometric absorption methods have been used, whereas, for cation exchange column, in addition to the spectrophotometric absorption method, a radioactive $^{51}\text{Cr}^{3+}$ solution has been used to determine the elution curve for the different Cr^{3+} species. Section 2.4 presents the details of all the experiments carried out using TNI K_2CrO_4 , Na_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Cr}_2\text{O}_7$ and chromic nitrate. Section 2.5 gives a brief description of the

principles of detection and measurement of γ -radiation, and the details of the scintillation counting assembly used in this study.

Chapter III presents the experimental data and has again been subdivided into five sections. Results of the experiments carried out, respectively, with K_2CrO_4 , Na_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Cr}_2\text{O}_7$ and chromic nitrate, are presented in Sections 3.1, 3.2, 3.3, 3.4 and 3.5.

Chapter IV is divided into three subsections. General trends of the experimental results, effects of the medium of dissolution and their time-variation are discussed in Section 4.1. Section 4.2 gives the significance and some probable interpretations of these results. A theoretical model has been proposed for calculation of the yield of $^{51}\text{Cr}^{6+}$ -species based on the relative probability of collision of a recoil $^{51}\text{Cr}^{6+}$ with O^{2-} ions in Section 4.3.

In conclusion, it has been found, for chromates and dichromates under investigation, that:

- (a) The yields decrease in the following order in the different media:
 (distilled water without added carrier) > (1N H_2SO_4 with excess Cr^{6+} carrier) > (1N H_2SO_4 containing excess of both Cr^{3+} and Cr^{6+} carriers) > (1N H_2SO_4 containing excess of Cr^{3+} carrier).
- (b) There is a time-variation of the yield of Cr^{6+} in solution which is most prominent in the case of K_2CrO_4 .

- (c) The yield of Cr^{3+} -monomer (M) increases with time while that of Cr^{3+} -dimer and -polymer (DP) always decreases with time.
- (d) Since milligram quantities of TNI sample are dissolved in every case, there is automatic addition of milligram quantities of Cr^{6+} carrier. The fact that there is considerable decrease of Cr^{6+} with time in the case of TNI K_2CrO_4 indicates the presence of macroscopic amount of reducing agent(s).
- (e) The marked time-variation in the case of TNI K_2CrO_4 possibly explains the variation in the results reported by other authors who did not consider time as an experimental parameter.
- (f) A good correlation exists between the $^{51}\text{Cr}^{6+}$ yield and the relative probability of collision between a recoil $^{51}\text{Cr}^{6+}$ and O^{2-} ions. An extension of this idea leads to the prediction of the yields of $^{51}\text{Cr}^{6+}$ in a mixed crystal of K_2CrO_4 and K_2BeF_4 containing varying mole percent of K_2CrO_4 .

Chapter V summarizes the results of the present investigation.

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CHAPTER I

INTRODUCTION

The present work consists, principally, of a detailed investigation of the experimental conditions of analysis on the relative yields of Cr^{6+} , Cr^{3+} (monomer) and Cr^{3+} (dimer and polymer) in solutions of thermal neutron irradiated sodium and potassium chromates and dichromates. This work belongs to the broad area of chemical effects of nuclear transformation which came into being when Szilard and Chalmers⁽¹⁾ made their remarkable observation on neutron irradiated $\text{C}_2\text{H}_5\text{I}$ in 1934. These scientists found that a large fraction of the ^{128}I formed by the reaction $^{127}\text{I} (n, \gamma) ^{128}\text{I}$ was in the form of elemental iodine. This fact signified that the nuclear transformation $^{127}\text{I} (n, \gamma) ^{128}\text{I}$ was accompanied by a chemical effect as shown by the breaking of some C-I bonds of $\text{C}_2\text{H}_5\text{I}$. Amaldi et al.⁽²⁾ explained this phenomenon on the basis of the conservation of momentum between the emitted γ -ray and the recoiling product nucleus. The capture of a thermal neutron releases energy equal to the neutron binding energy (~ 8 MeV) which raises the product nucleus to an excited level. De-excitation occurs through the emission of large-quantum gammas as well as cascades of gammas of small quantum energies. In the latter case the average resultant momentum

of the recoil nucleus can be calculated on the basis of uncorrelated γ -emission and may turn out to be smaller than that due to any single γ -ray in the cascade. For a single γ -ray emission, the recoil energy in units of electron volts is given by

$$E_r = \frac{537 E_\gamma^2}{M} \quad (\text{eV})$$

where E_γ = gamma ray energy in units of MeV and M = mass number of the recoiling nucleus. Thus, even a 1 MeV gamma, emitted by ^{128}I would impart a recoil energy of 4.2 eV which would be sufficient to break the C-I bond, the bond energy being only 2.0 eV. Whenever a nuclear reaction undergone by an atom in a chemical compound is accompanied by an average recoil energy of the product atom greater than the total energy of all the bonds that held the reactant (in terms of nuclear reaction) atom in place in the original compound, one would expect a chemical change. One of the challenging tasks before the investigators in this field over the last few decades has been to explain why experimentally one finds apparently much fewer bonds broken during a nuclear reaction where, theoretically, not a single bond is expected to survive. In liquid phase studies it is found that about 20% of ^{128}I remains as organic compound^(3,4), while gas phase studies⁽³⁾ have shown that in the case of neutron irradiated $\text{C}_2\text{H}_5\text{Br}$ at 3 μm pressure less than 1% of $^{80\text{m}}\text{Br}$ ($t_{1/2} = 4.4$ hrs) remained in organic combination. In solid

phase, on the other hand, the percentage of ^{80m}Br in organic combination was shown by Friedman and Libby⁽⁵⁾ and Fox and Libby⁽⁶⁾ to go up from 39% to 88% in the case of irradiated n-propyl bromide. This fact points to a possible effect of density and perhaps of the crystalline character of the solid as compared to the liquid. Further, a few experiments using constant temperature high density gas phase, showed⁽⁷⁾ an increase in the organic yield in the case of CF_3Br irradiated with neutrons.

In the case of inorganic salts, a large number of studies have been made using crystalline salts containing oxy-anions. The (n, γ) reaction on the metal atom usually yields a considerable fraction of the radioactivity in the higher oxidation state of the metal which was present in the original oxy-anion form and the rest in lower oxidation states. The percentage of radioactivity in the original anionic form is known as "retention". One of the best studied systems is that comprising of chromates and dichromates. ^{50}Cr has a high cross section for $^{50}\text{Cr} (n, \gamma) ^{51}\text{Cr}$ reaction with thermal neutrons and the product ^{51}Cr has a convenient half-life of 27.8 days, decaying to ^{51}V with the emission of EC X-rays of 320 KeV. Numerous studies⁽⁸⁾ have been made on the percentage of retention under a variety of experimental conditions, and, in particular, when annealing is carried out. Williams and Coworkers^(9,10) found that retention increases with increasing pile exposure of the sample. On the other

hand, Green and Maddock⁽¹¹⁾ found that heating of an irradiated sample of K_2CrO_4 increases retention. These "back reactions" leading to increased yield of the radioactive atom in the original state of oxidation are known as "annealing" which may be induced either thermally or by radiation exposure. Annealing studies yield some information on the activation energies involved in recombination and, if such studies are carried out while the crystalline environment is artificially altered in a controlled manner, one may hope to have some understanding of the primary distribution of the initial species produced in the irradiated crystals. A very large number of studies on annealing of irradiated chromate system has been carried out till now⁽¹²⁻¹⁵⁾.

The basic experimental data on all such studies are obtained by separating the various species having different oxidation states after dissolving the irradiated sample in some liquid medium which mostly happens to be water. Since the process of dissolution inevitably involves interaction between the primary species present in the crystal and the molecules of the solvent it is highly probable that there may not be any direct correspondence between the distribution (i.e., the relative yields of the various species in different oxidation states) as seen after dissolution and separation of the species by chemical or other means and the original one present in the irradiated crystal.

This is more so because of the large number of defects produced in the crystals during irradiation. On dissolution, trapped electrons and holes would be liberated producing a host of reducing and oxidizing species like the hydrated electron, OH and H_2O_2 in the case of water as the solvent^(16,17). In aqueous solutions, therefore, both oxidation and reduction processes may proceed simultaneously from the moment of dissolution and it is essential to study the variation in the distribution of the radioactive species among its various oxidation states as a function of time after dissolution of the irradiated sample in aqueous media under different experimental conditions. The need for such studies is amply borne out in the case of the distribution of ^{35}S obtained from $^{35}Cl(n,p)^{35}S$ reaction with thermal neutrons. Conflicting results have been reported in the literature and a comparatively recent work by Muddukrishna and Mukherji⁽¹⁸⁾ showed that these may be ascribed to ongoing, possibly radiolytic, reactions in solution and that reproducible patterns of ion-exchange chromatographs can be obtained if analysis is carried out at a predetermined time after dissolution of the sample. This work represents an investigation of a similar nature in the case of chromates and dichromates of sodium and potassium. As has been already stated, for chromates and dichromates, most authors, particularly in recent times, have directed their efforts towards annealing studies and few in-depth and fundamentally detailed studies on the effects of different conditions of dissolution,

particularly that of the time elapsed between the dissolution and analysis of the sample, on the distribution patterns have been carried out. Such studies need comparatively clean techniques requiring the addition of a minimum number of reagents, quick in terms of sample withdrawal and completed separation of the different species, and, capable of yielding convincingly reproducible results. Some authors⁽¹⁹⁻²¹⁾ have reported on the effects of the presence of particular carriers and their relative concentrations at the time of dissolution of a TNI sample in media of different acidity. Since it is impossible to distinguish between the Cr^{6+} or Cr^{3+} -monomer coming directly from the irradiated sample and those generated by possible secondary reactions in solution, it is necessary to protect the radioactive species by isotopic dilution with a large excess of carriers of the different species. The present work has been carried out with these aims in view.

CHAPTER II

EXPERIMENTAL

2.1 General Considerations

In 1947, Muxart et al.⁽²²⁾ were the first to investigate thermal neutron irradiated potassium dichromate system using a chemical precipitation method. The irradiated dichromate was dissolved in water containing Cr(III)-sulphate as a carrier; Cr(III) was precipitated as $\text{Cr}(\text{OH})_3$. The activity of $\text{Cr}(\text{OH})_3$ precipitate gave the yield of $^{51}\text{Cr}(\text{III})$. The total activity of a portion of the irradiated dichromate solution was measured and the yield of $^{51}\text{Cr}(\text{VI})$ was determined from the difference of the two activities.

Since then, a variety of analytical techniques has been developed^(19,23-44) in order to determine the distribution of ^{51}Cr mainly in two of its most stable oxidation states, Cr(VI) and Cr(III). The following are some of the most widely used techniques: (i) separate chemical precipitations of Cr(III)^(19,25-29) and Cr(VI)^(19,23-25), (ii) adsorption on alumina column⁽³⁰⁻³²⁾, (iii) anion⁽³³⁻³⁶⁾ and cation^(37,38,44) exchange chromatographies. Besides these, solvent extraction^(39,40) and electrophoretic⁽⁴¹⁾ methods have also been used.

Further, several chemical analytical procedures were used to detect the possible presence of the relatively unstable species Cr(II) in air-free solutions of neutron irradiated chromates^(20,45). In these studies, Cr(II) was converted

into Cr(II)-oxalate complex, oxidized to Cr(III)-oxalate and then separated from other species by cation exchange chromatography.

Schematic representations of some of these analytical procedures (19,23-29,33-37,44), are shown in Figures 2.1-1 to 2.1-4.

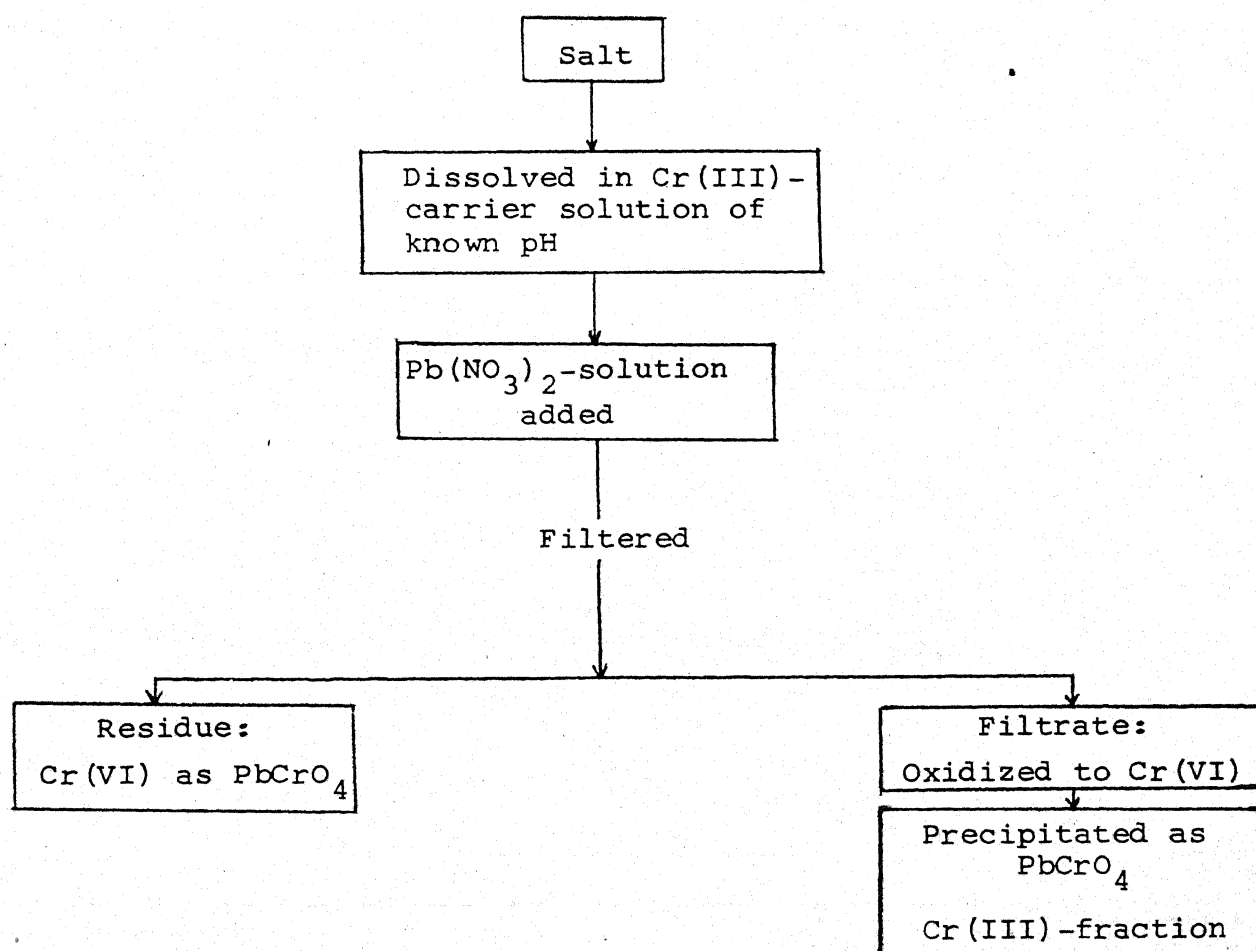


Fig. 2.1-1 : Scheme of separation of ^{51}Cr into Cr(VI) and Cr(III) using PbCrO₄ precipitation method.

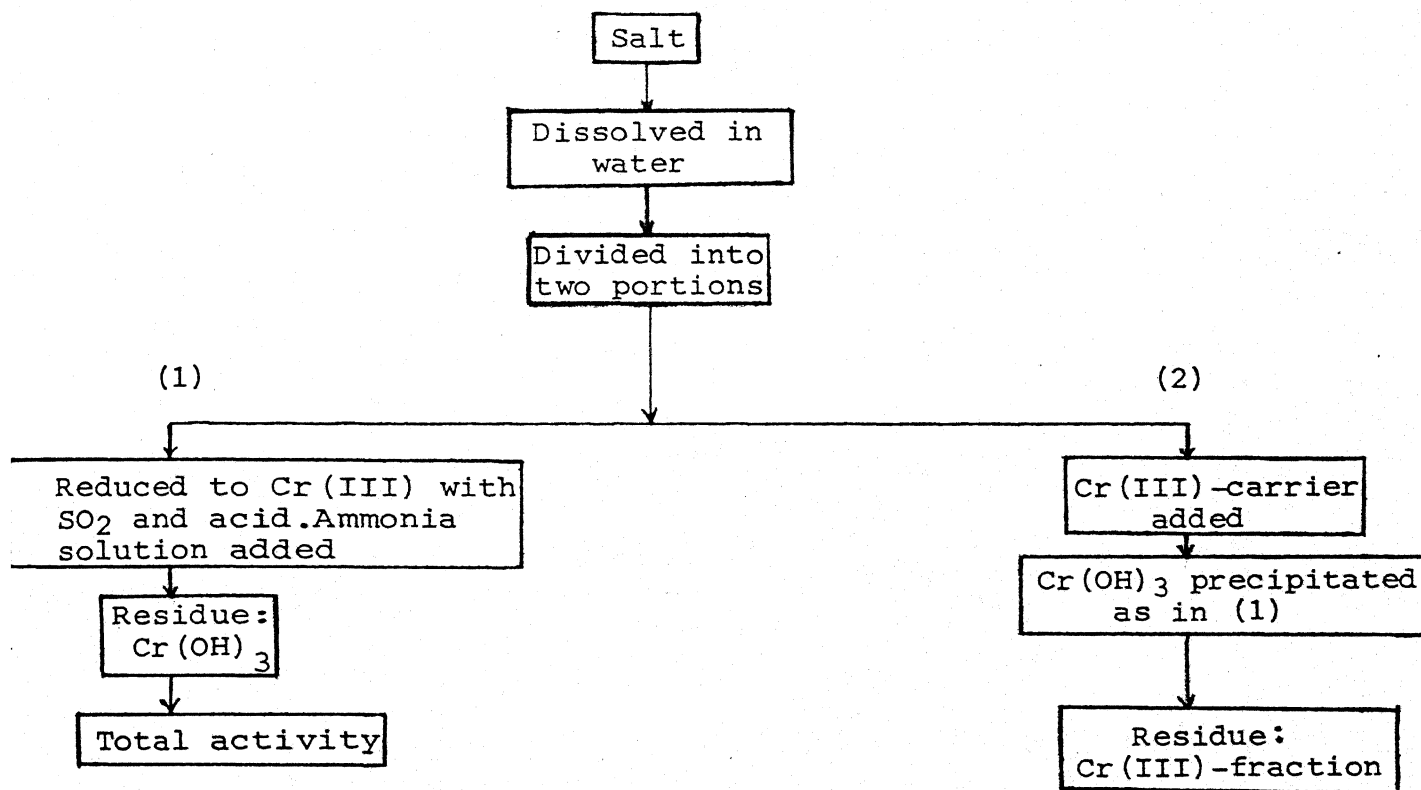


Fig. 2.1.-2 : Scheme of separation of ^{51}Cr into Cr(VI) and Cr(III) by Cr(OH)_3 precipitation method

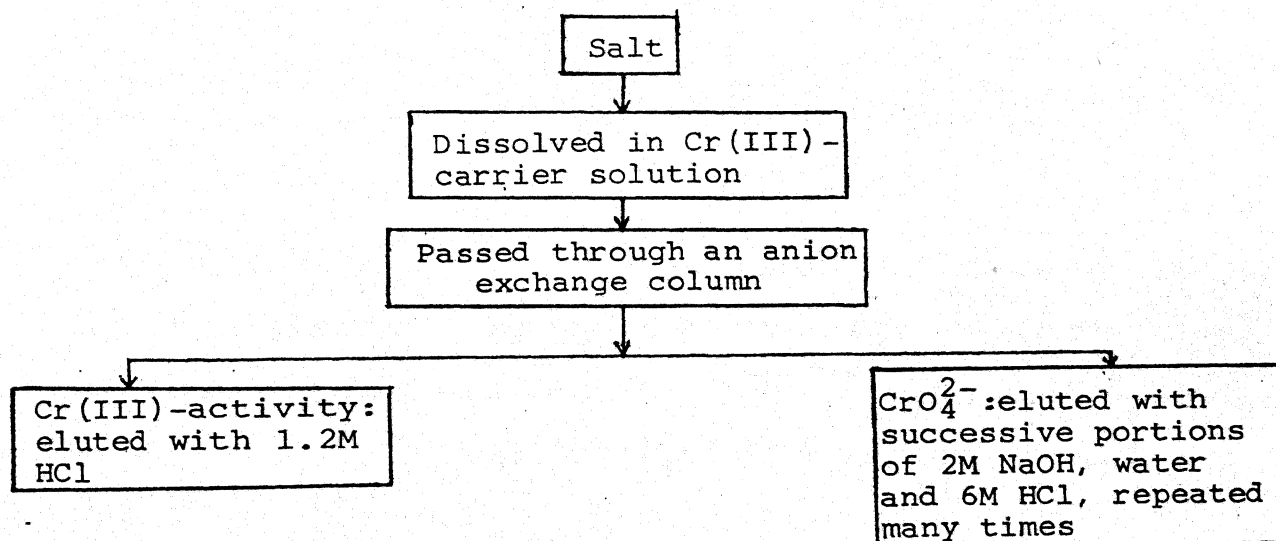


Fig. 2.1-3 : Scheme of separation of ^{51}Cr into Cr(III) and Cr(VI) by anion exchange chromatography

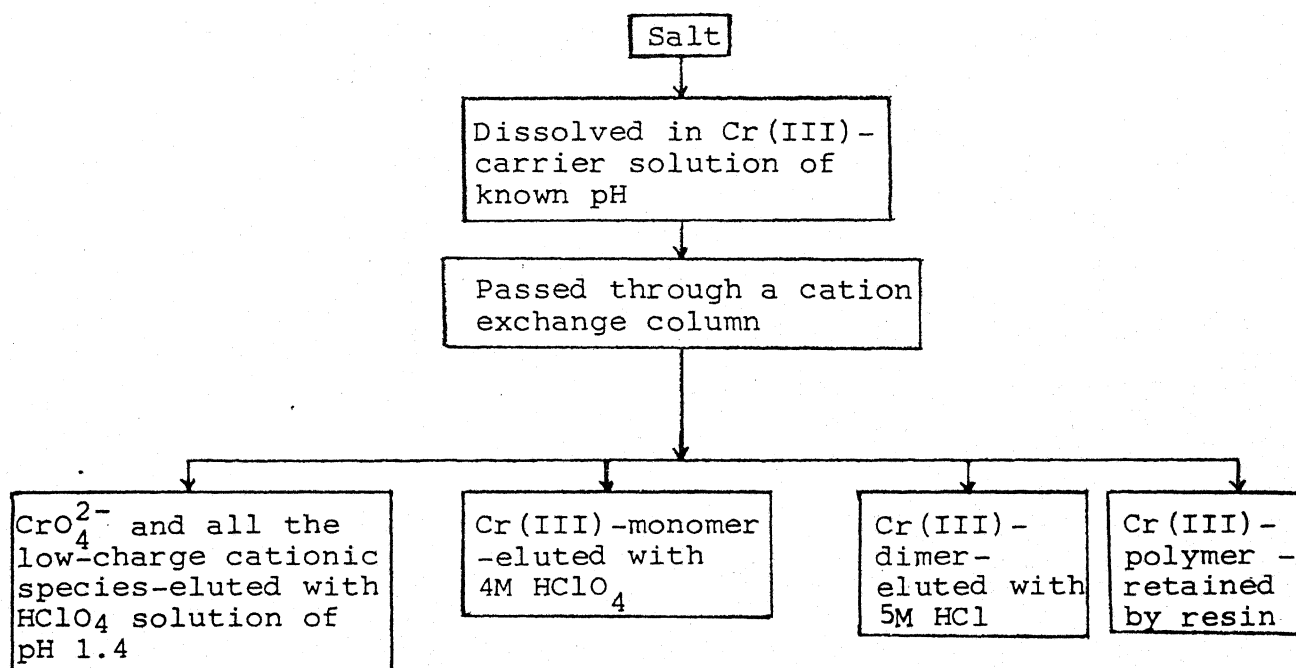


Fig. 2.1-4 : Scheme of separation of ^{51}Cr into Cr(VI) and Cr(III) by cation exchange chromatography

The results obtained using the above techniques are often found to be irreproducible. It was later suggested⁽⁴⁶⁾ that quantitative errors may have been made in at least some of these measurements, although most qualitative observations were possibly valid.

Several authors have suggested some explanations for these observed discrepancies. A number of factors, like, (a) irradiation temperature^(12,25,47-50), (b) storage temperature^(12,25,47,50), (c) neutron dose and ionizing radiation dose^(12,47,51), (d) crystal structure and form^(19,26,27), etc., have been held responsible for the observed variation

in the distribution of ^{51}Cr between two of its most stable oxidation states, i.e., +3 and +6. In the case of chemical separations, the pH of the solvent has also been reported to affect the distribution^(19,46).

Different thermal neutron induced primary species produced in an inorganic crystal, like that of a chromate or a dichromate, can not be identified in the solid state by any direct physical method. During irradiation many defects are produced inside a crystal. There is hardly any physical method which would not require either heating or exposure of the sample to radiation, both of which are known to cause interactions between the primary species and trapped electrons, thus changing the oxidation state of the former.

Chemical methods do not give any direct indication as to the nature of the species in the solid state. Chemical analysis requires dissolution of the sample in a solvent and subsequent treatment with various reagents. At the time of dissolution and during the separation process the primary species present in the neutron irradiated crystal interacts with the solvent and the other reagents used. Due to these complications identification of the primary species becomes extremely difficult. Still, because of their relative simplicity, different chemical methods have been chosen by most authors, although, the identification of the primary

species becomes highly speculative in this case.

In the present investigation, we have used short-column ion-exchange chromatography as the method of analysis. The choice of the method was based on the following considerations: (i) Muddukrishna and Mukherji⁽¹⁸⁾ reported the existence of a dynamic situation in solutions of thermal neutron irradiated chlorides and observed a variation in the relative proportions of different S-anions present in the solution with time and, hence, the time interval between the dissolution of the irradiated salt and the final chemical separation step is an important experimental parameter. To carry out a series of chemical separations within a short period of time, in chromate systems, a short-column technique was found to be very convenient and efficient. (ii) Any unstable species present at the time of dissolution might get adsorbed on the ion exchanger and would appear in a different elution region than those of the known species. If the separation is completed fast enough, its chemical form could possibly be identified before it has time to react completely. (iii) In ion exchange chromatography, only a few reagents are used during the whole process, namely, the eluent(s) and the solvent with or without carrier(s). Therefore, the chances of interaction between the primary species and the added reagents is considerably reduced.

2.1-1 Planning and Sequence of the Present Experiments

In the present investigation, an attempt has been made to find out, as far as possible, the "true" distribution of ^{51}Cr among Cr^{6+} , Cr^{3+} -monomer and Cr^{3+} -dimer and -polymer, or their precursors, as is present at the moment of dissolution, and its variation with time. Separation of the various ^{51}Cr -species has been carried out using both short-column anion and cation exchange chromatographies. An attempt has also been made to detect any neutral ^{51}Cr -species at the time of dissolution. The aim of the time-based study of the ^{51}Cr -distribution in aqueous solutions was to observe possible trends of reactions of the ^{51}Cr -species in solution, which, by extrapolation, could yield information about the distribution in the irradiated crystal.

The following different types of experiments were carried out with chromates and dichromates of sodium and potassium. The neutron irradiated sample was dissolved in:

- (i) distilled water without added carrier,
- (ii) 0.01N H_2SO_4 without added carrier,
- (iii) 1N H_2SO_4 without added carrier,
- (iv) 1N H_2SO_4 containing large excess of Cr^{6+} -carrier (1g of Na_2CrO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7/2$ ml),
- (v) 1N H_2SO_4 containing Cr^{3+} -carrier (500 mg of potassium chrome alum/2 ml),
- (vi) 1N H_2SO_4 containing both Cr^{6+} (1g of Na_2CrO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7/2$ ml) and Cr^{3+} (500 mg of potassium chrome alum/2 ml) carriers.

The object of experiment (i) was to minimize the chances of interaction of a particular ^{51}Cr -species with the added reagents so that ^{51}Cr -distribution obtained under this condition should be somewhat uncomplicated and presumably the observed distribution would be closest to the original one. No time-based experiment could be performed with distilled water alone as the medium of dissolution since the carrierless $^{51}\text{Cr}^{3+}$ -activity was getting adsorbed on the glass walls of the test tube.

Since the neutron irradiated samples are Cr^{6+} salts, the solutions of irradiated salts automatically contain milligram quantities of Cr^{6+} -carrier. The results of the experiments (ii) and (iii) show a considerable time-variation in ^{51}Cr -distribution with a decrease in the yield of Cr^{6+} -species which indicate that a macroscopic effect is probably involved by which Cr^{6+} -species gets reduced in solution to Cr^{3+} -monomer (since Cr^{3+} -monomer yield increases) even in presence of milligram quantities of Cr^{6+} -carrier. If a macroscopic effect is at work, then a large excess of Cr^{6+} -carrier should be able to prevent the reduction of Cr^{6+} into Cr^{3+} -species. Keeping this point in mind, experiment (iv) was carried out by dissolving the sample in 1N H_2SO_4 containing a large excess of Cr^{6+} -carrier. The results of these experiments supported the above expectation, since the time-variation of $^{51}\text{Cr}^{6+}$ -species was found to be negligible under

this condition.

Experiment (v) was performed in order to find out the effect of Cr^{3+} -carrier on ^{51}Cr -distribution at the time of dissolution. Since the only Cr^{3+} salt available was potassium chrome alum which could be used as a carrier, it was impossible to carry out the experiment in the presence of a "large excess" of Cr^{3+} -carrier. A maximum of about 500 mg of the Cr^{3+} salt could be dissolved in 2 ml of 1N H_2SO_4 which corresponded to about 25 mg of Cr^{3+} -carrier per millilitre of the solution.

Experiment (vi) was performed basically to observe the effect of the presence of both Cr^{6+} and Cr^{3+} -carriers in excess at the time of dissolution and, if possible, to correlate the observed ^{51}Cr -distribution to the original one at the instant of dissolution.

Besides these, two experiments were carried out with TNI $\text{K}_2\text{Cr}_2\text{O}_7$ dissolved in 1N H_2SO_4 at 0°C and 90°C , respectively, and two experiments, with TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ dissolved in dried dimethyl formamide in nitrogen atmosphere and in ordinary atmosphere, respectively, to observe the effect of temperature in the former case and of a non-aqueous solvent in the latter on the distribution of ^{51}Cr -species.

The details of these experiments are given in section 2.4.

A set of experiments has been carried out with TNI chromium nitrate, where the sample was dissolved

in (i) distilled water, (ii) 1N H_2SO_4 , (iii) 1N H_2SO_4 containing Cr^{6+} -carrier in milligram quantities, (iv) 1N H_2SO_4 containing a large excess of Cr^{6+} -carrier, (v) an alkaline solution of $^{51}\text{CrO}_4^{2-}$, and (vi) 1N H_2SO_4 containing n-irradiated K_2CrO_4 .

The main object of these experiments was to ascertain the presence or absence of Cr^{6+} -species when an irradiated Cr^{3+} salt is dissolved in an aqueous medium. No ^{51}Cr was found in the form of Cr^{6+} -activity in these experiments, but a large amount of activity was obtained as a neutral ^{51}Cr -species.

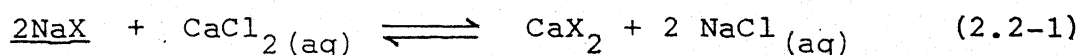
The details of the experiments carried out with TNI chromium nitrate are given in section 2.5.

2.2 Principles of Ion-exchange Chromatography

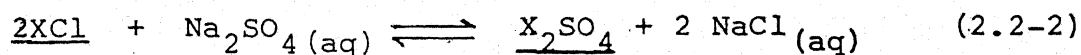
Chromatography is a technique which allows separation of mixtures according to different rates of migration of its components. Originally chromatography was developed for the separation of organic compounds on alumina and activated charcoal, and has been extended to include paper, gas, partition and ion exchange chromatographies. The basic principles and the theories are the same for all. Since ion exchange chromatography has been used as the method of analysis in the present investigation we shall confine our discussion to this technique based on the references - (52-55).

An ion exchanger is an insoluble solid material which carries exchangeable cations and anions. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign when the ion exchanger is in contact with an electrolyte solution. Carriers of exchangeable cations are called cation exchangers, and those of exchangeable anions, anion exchangers. Certain materials are capable of both cation and anion exchange — these are called amphoteric ion exchangers.

A typical cation exchange is



and a typical anion exchange is



where X represents a structural unit of the ion exchanger and the type of charge associated with X is called the fixed charge. Solid phases are underlined and (aq) indicates that the electrolyte is in the aqueous phase. The exchangeable ions in both phases are called counter ions; the fixed charge and the ions of the electrolyte having the same sign as fixed charge are called the co-ions. In Eq. 2.2-1 Na^+ and Ca^{2+} are the counter ions whereas Cl^- ions are the co-ions. In Eq. 2.2-2, Cl^- and SO_4^{2-} are the counter ions

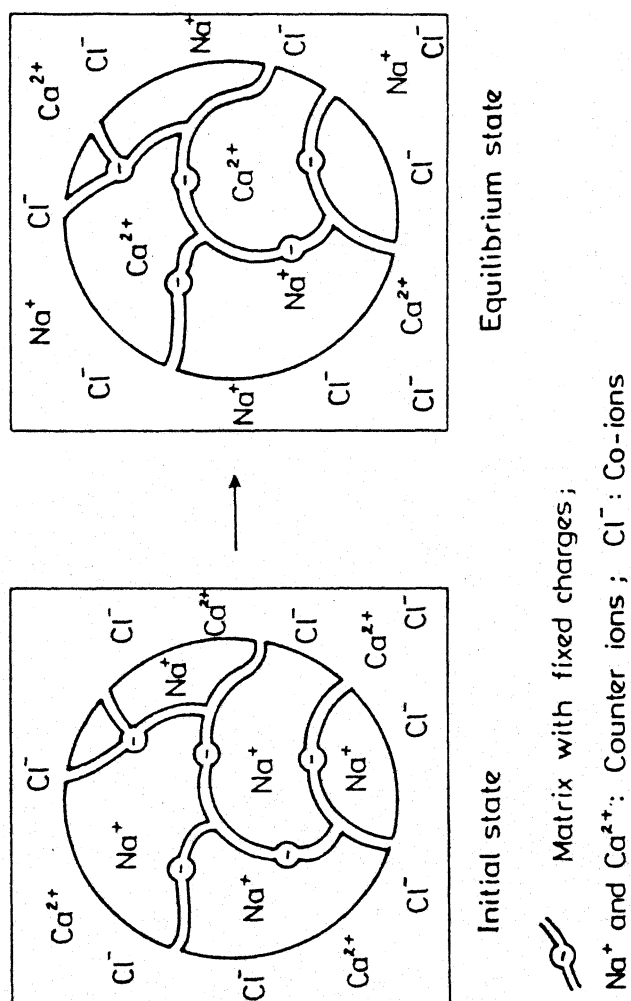


Fig.2.2-1 Schematic representation of a cation exchange process when a cation exchanger containing counter ions Na^+ is placed in a solution containing counter ions Ca^{2+} (left). The counter ions are redistributed by diffusion until equilibrium is attained (right).

and Na^+ ions the co-ions. Figure 2.2-1 shows the schematic representation of Eq. 2.2-1.

An ion exchanger containing, say, exchangeable Na^+ ion is said to be in the Na^+ form. In the process represented by Eq. 2.2-1, the cation exchanger is originally in the Na^+ form, and is "converted" into the Ca^{2+} form. When complete conversion takes place the ion exchanger becomes "exhausted" and can be "regenerated" with a solution of Na^+ salt. In regeneration process Eq. 2.2-1 is reversed.

The counter ion content of the ion exchanger is called its "ion exchange capacity". This quantity is a constant determined by the magnitude of the framework charge and is independent of the nature of the counter ion.

As a rule, the pores are occupied not only by the counter ions but also by the solvent and solutes which can enter the pores when the ion exchanger is in contact with a solution. The uptake of the solvent may result in a swelling of the ion exchanger. The uptake of the solutes is usually called "sorption", though it is essentially a distribution of the solute between the two liquid phases, namely, the pore liquid and the solution outside. The sorbed counter ions are also accompanied by an equivalent amount of mobile co-ions from the electrolyte solution in order to maintain electroneutrality. Thus, the counter ion content of an ion exchanger not only depends on the

magnitude of the framework charge, but also on its co-ion content. The common definitions of ion exchange capacities refer to ion exchangers which are free of co-ions.

When the cation exchanger (containing no sorbed electrolyte) is placed in a dilute solution of a strong electrolyte, there is considerable concentration difference between the two phases. The cation concentration is larger in the ion exchanger, whereas the (mobile) anion concentration is larger in the solution. If the ions carried no electrical charges, these concentration differences would be levelled out by diffusion. However, such a process would disturb the electroneutrality since, actually, the ions are charged. Migration of cations into the solution, or of anions into the ion exchanger results in an accumulation of positive charge in the solution and of negative charge in the ion exchanger. The first few ions which diffuse thus build up an electric potential difference between the two phases. This so called "Donnan potential" pulls cations back into the ion exchanger and anions back into the solution.

The situation with anion exchangers is analogous. Here, of course, the Donnan potential has the opposite sign.

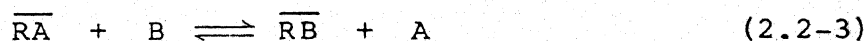
The Donnan potential has one immediate consequence for electrolyte sorption: it repels co-ions from the ion exchanger phase and thus prevents the internal co-ion

concentration from rising beyond an equilibrium value which is usually much smaller than the concentration in the external solution.

As shown in the Fig. 2.2-1, at equilibrium, the ion exchanger as well as the solution contain both the counter ion species Na^+ and Ca^{2+} . The concentration ratio of the two counter ions, however, is not necessarily the same in both the phases. As a rule, the ion exchanger prefers one species over the other. The preference for one species may have several causes. The most important of these are: (a) the electrostatic interaction between the charged framework and the counter ions depend on the size and the valence of the counter ion, and (b) large counter ions may be sterically excluded from the narrow pores of the ion exchanger.

These effects depend on the nature of the counter ion and thus may lead to preferential uptake of a species by the ion exchanger. The ability of the ion exchanger to distinguish between various counter ion species is called the "selectivity". The selectivity of an ion exchanger for counter ions is expressed in terms of the selectivity coefficient which is defined as follows:

In general, an ion exchange process can be written as,



where A and B are the counter ions with appropriate charges which have been taken as unity here. The equilibrium constant for the process is given by,

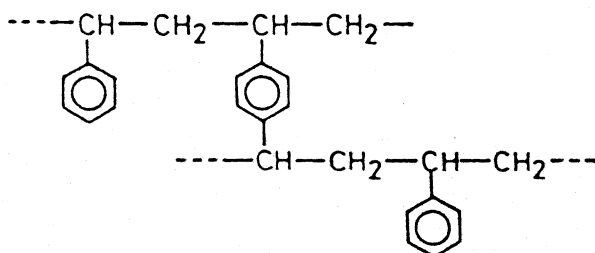
$$\begin{aligned}
 K &= \frac{a_{\overline{RB}} \cdot a_A}{a_{\overline{RA}} \cdot a_B} = \frac{[\overline{RB}][A]}{[\overline{RA}][B]} \cdot \frac{\gamma_{\overline{RB}} \cdot \gamma_A}{\gamma_{\overline{RA}} \cdot \gamma_B} \\
 &= K_A^B \cdot \frac{\gamma_{\overline{RB}} \cdot \gamma_A}{\gamma_{\overline{RA}} \cdot \gamma_B} \quad (2.2-4)
 \end{aligned}$$

where a and γ with appropriate subscripts stand for the activity and the activity coefficient, and the terms within the square brackets represent concentrations. K_A^B is termed the "selectivity coefficient" since it measures the tendency of the exchanger to select B over A.

If $K_A^B > 1$, then the exchanger selects ion B and if $K_A^B < 1$, the exchanger shows selectivity for A.

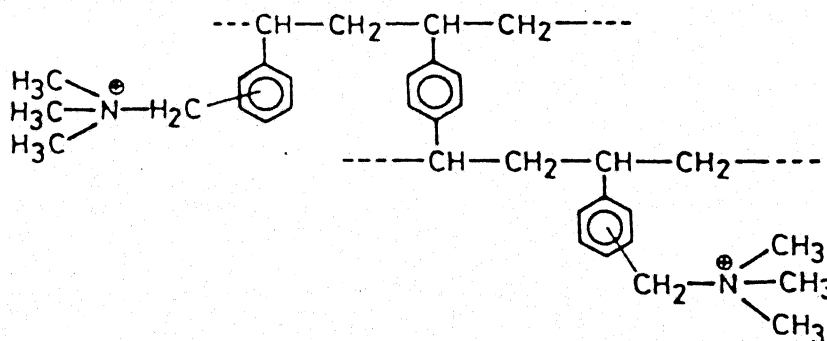
Structurally the common feature of all natural and synthetic ion exchangers is a framework with electric surplus charge and mobile counter ions. In the present study, organic ion exchange resins have been used. The framework or the 'matrix' consists of an irregular, macromolecular, 3-dimensional network of hydrocarbon chains. The matrix carries ionic groups such as $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3^{2-}$, AsO_3^{2-} in

cation exchangers and $-\text{NH}_3^+$, >NH_2^+ , $-\text{NH}^+$, >N^+ , >S^+ , etc., in anion exchangers. The matrix is a crosslinked polystyrene as shown below.

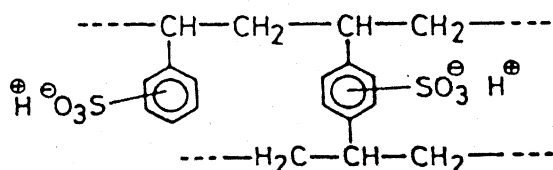


Suitable cationic or anionic functional groups are introduced to obtain a particular resin.

In the present experiments, Dowex 1X8 and Dowex 50WX8 were used as anion and cation exchange resins respectively. Dowex 1 has a quaternary ammonium radical as the functional group making it a strong-base resin. The structure is shown below:



Dowex 50 cation exchange resin is crosslinked polystyrene with sulphonic acid groups:



One particle of an ion exchange resin is practically a single macromolecule. The resins are insoluble in all solvents (by which they are not destroyed) because of their crosslinking. The degree of crosslinking determines the mesh width of the matrix and thus the swelling ability of the resin and the mobilities of the counter ions in the resin. The latter, in turn, determines the rates of ion exchange of the resin. The average mesh width of highly crosslinked resins is of the order of only a few angstrom units. The mesh width of very weakly crosslinked and swollen resins may exceed 100\AA .

2.3 Procedure

2.3-1 Materials

(a) Ion Exchange:

For experiments using ion exchange columns 100-200 mesh anion exchanger (Dowex 1X8 in the chloride form having

a total exchange capacity of 2.4 m eq/ml on the dry basis and 1.2 m eq/ml on the wet basis) and cation exchanger (Dowex 50WX8 in the hydrogen ion form having a total exchange capacity of 5.1 m eq/ml on the dry basis and 2.0 m eq/ml on the wet basis) were used.

The eluents used were analar grade HCl (0.5 M and 2.0 M) for cation separation and analar grade NaNO_3 (0.25 M solution) for anion separation.

(b) Samples for Irradiation:

Both Cr(VI) and Cr(III) samples were irradiated by thermal neutrons. Commercially available crystals of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$ and K_2CrO_4 were used after appropriate treatments described in section 2.3-2, while Na_2CrO_4 and $\text{Cr}(\text{NO}_3)_3$ were prepared in the laboratory, the details of which are provided in section 2.3-2. All the commercial samples used were of analar grade.

(c) Samples Used for Calibration of the Ion Exchange Columns:

For cation exchanger, the calibration curves were obtained using two different procedures. (a) Non-radioactive Cr^{3+} was adsorbed on the column and eluted. Spectrophotometric method was used to detect the concentration of Cr^{3+} in successive aliquots of the eluate. Samples used for the calibration using this method, i.e., $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ and $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$,

were prepared in this laboratory^(56,57), the details are given in section 2.3-2; (b) Radioactive sample of $^{51}\text{Cr}^{3+}$ was added to the column and measuring the radioactivity of the successive aliquots of the eluate. The radioactive $^{51}\text{Cr}^{3+}$ was obtained from the Isotope Group, Bhabha Atomic Research Centre, Bombay, India, in the form of a solution of $^{51}\text{Cr}(\text{III})$ in dil. HCl and the total strength of the solution was 5 mCi.

For anion exchange, analar grade K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ were used to obtain calibration curves for $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} using (a) precipitation and (b) spectrometric methods.

2.3-2 Preparation of Samples for Irradiation

Crystals of analar grade K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ were crushed, powdered and stored in a desiccator before sealing.

Anhydrous crystals of $\text{Na}_2\text{Cr}_2\text{O}_7$ were prepared from analar grade $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ by heating the powdered crystals of the latter at 105°C for about five hours in an air oven. The product was stored in a vacuum desiccator.

Preparation of anhydrous Na_2CrO_4 : A solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ was treated with excess of NaOH solution and Na_2CrO_4 was precipitated by adding excess of ethyl alcohol. The precipitate was filtered and washed repeatedly with ethyl alcohol to remove excess of NaOH. The residue was then dried to constant weight under an IR lamp for about three

hours to obtain anhydrous Na_2CrO_4 , which was finally stored in a vacuum desiccator.

Preparation of chromic nitrate⁽⁵⁶⁾: Chromic hydroxide was first precipitated from a solution of chrome alum by adding NH_4OH solution. The precipitate was filtered and washed repeatedly till the washings were colourless. The precipitate was dissolved in dilute nitric acid and was allowed to stand for a few days when purple crystals of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ appeared. The crystals were powdered and stored in a desiccator.

Sealing of the Samples:

20 mg of each sample (Na_2CrO_4 , K_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$ and chromium nitrate) was taken in a quartz ampoule, of length 1.5 inches and diameter 6 mm, sealed at one end. The open end of the ampoule was then attached to a quartz tube (Fig. 2.3-1) which was connected to a vacuum system. This set-up allowed us to seal a large number of samples under identical conditions. The samples were sealed at a pressure of 0.6-0.8 micron, after which the ampoules measured one inch in length.

Irradiation of the Samples:

The samples were irradiated with thermal neutrons in the CIRUS reactor at Bhabha Atomic Research Centre, Bombay, India. The details of the irradiation conditions are given in the Table 2.3-1 below. Henceforth, the Thermal Neutron

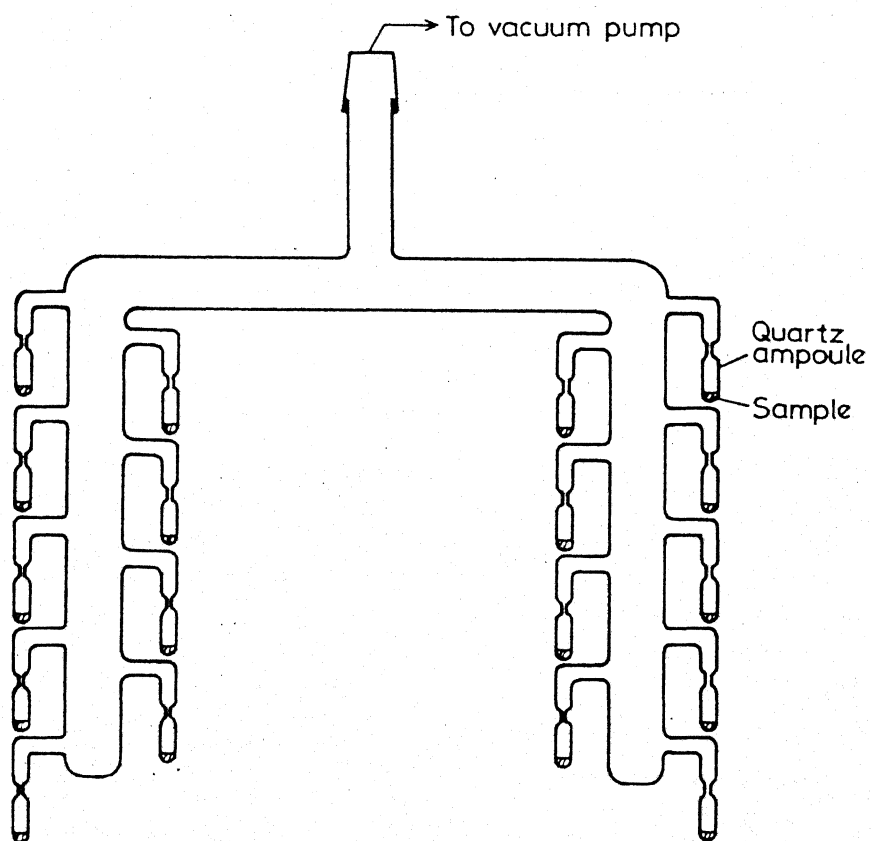


Fig.2-3-1 System for sealing several quartz ampoule at a time.

Irradiated samples will be designated as TNI samples.

Table 2.3-1 : The details of the neutron flux and the time of irradiation

Sample	Neutron flux in $n\text{ cm}^{-2}\text{ sec}^{-1}$	Irradiation time (hour)
Na_2CrO_4	1.0×10^{12}	12
K_2CrO_4	1.7×10^{12}	12
	1.0×10^{12}	
$\text{Na}_2\text{Cr}_2\text{O}_7$	1.0×10^{12}	12
$\text{K}_2\text{Cr}_2\text{O}_7$	1.0×10^{12}	12
$\text{Cr}(\text{NO}_3)_3$	1.7×10^{12}	12

2.3-3 Preparation of the Samples for Calibration

$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ were prepared^(56,57) for the calibration of the cation exchange column. $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ was made by boiling chromic anhydride with concentrated hydrochloric acid in the ratio 1:6. The solution was evaporated till its weight was little less than that of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and then distilled water was added till the weight became equal to that of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. Hydrogen chloride was then passed into the solution followed by the addition of ether when small emerald

green crystals of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ separated out.

A part of the above crystals was refluxed with water for half an hour. The flask was then cooled in an ice-salt mixture and HCl gas was introduced into it with stirring. When the mixture became saturated with HCl gas, a fine powder separated which was filtered out. The solid was dried under vacuum and then washed with acetone until the washings appeared colourless. When the traces of acetone evaporated the crude product was dissolved in water and saturated with HCl gas. The residue, $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, was filtered, washed with acetone and dried over sulphuric acid.

$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ was precipitated from the filtrate obtained from the above experiment by adding ether and passing hydrogen chloride into this at 10°C . The product was filtered and dried over sulphuric acid.

UV-visible absorption spectra were recorded for all these compounds in a Shimadzu UV 240 spectrophotometer. The following are the λ_{max} values obtained for the above complexes.

Table 2.3-2 : λ_{\max} Values for Cr(III)-Complexes

Compound	λ_{\max} (obs) (nm)	λ_{\max} (lit) (nm)	References
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$	287	284	(58)
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$	389	-	-
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	264	264	(59)

Absorption wave lengths for $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ were not found in the literature.

Drying of Dimethyl Formamide (DMF) (58):

Commercial grade DMF was purified by azeotropic distillation with benzene. A mixture of DMF and benzene in the ratio 10:1 was distilled in a Dean-Stark apparatus at atmospheric pressure and the water was separated out. The mixture was then distilled and benzene azeotrope was collected between 70-75°C. The residual solvent was shaken with powdered barium oxide and filtered. This was then distilled under reduced pressure. The distillate was stored over molecular sieves.

2.3-4 Preparation of the Ion Exchange Column

The column consisted of a glass cylinder of inner diameter 0.9 cm filled up to a height of 2 cm with the appropriate resin. The top of the glass column had a B-14 jacket, so that a reservoir containing the eluent with a B-14 cone at its lower end could be attached to it. This permitted a constant hydrostatic head of the eluent to be maintained. The column had a stop-cock at the lower part and a small plug of glass wool was loosely placed in the column between the stop-cock and the ion exchange resin. The schematic representation of the set-up is shown in Figure 2.3-2.

A slurry of the cation or the anion exchange resin was prepared by soaking the resin in 0.1N HCl for 12 hours to avoid further swelling of the resin in the column. The resin was washed with distilled water and poured into the column containing some distilled water to avoid formation of air bubbles. The excess water was drained out after the column was filled up to the required height (2 cm) with the resin. The column was washed repeatedly with distilled water to remove completely the traces of chloride and hydrogen ions respectively from the anion and the cation exchange columns. This was tested by treating fresh washings of the columns with silver nitrate solution and methyl orange indicator as required.

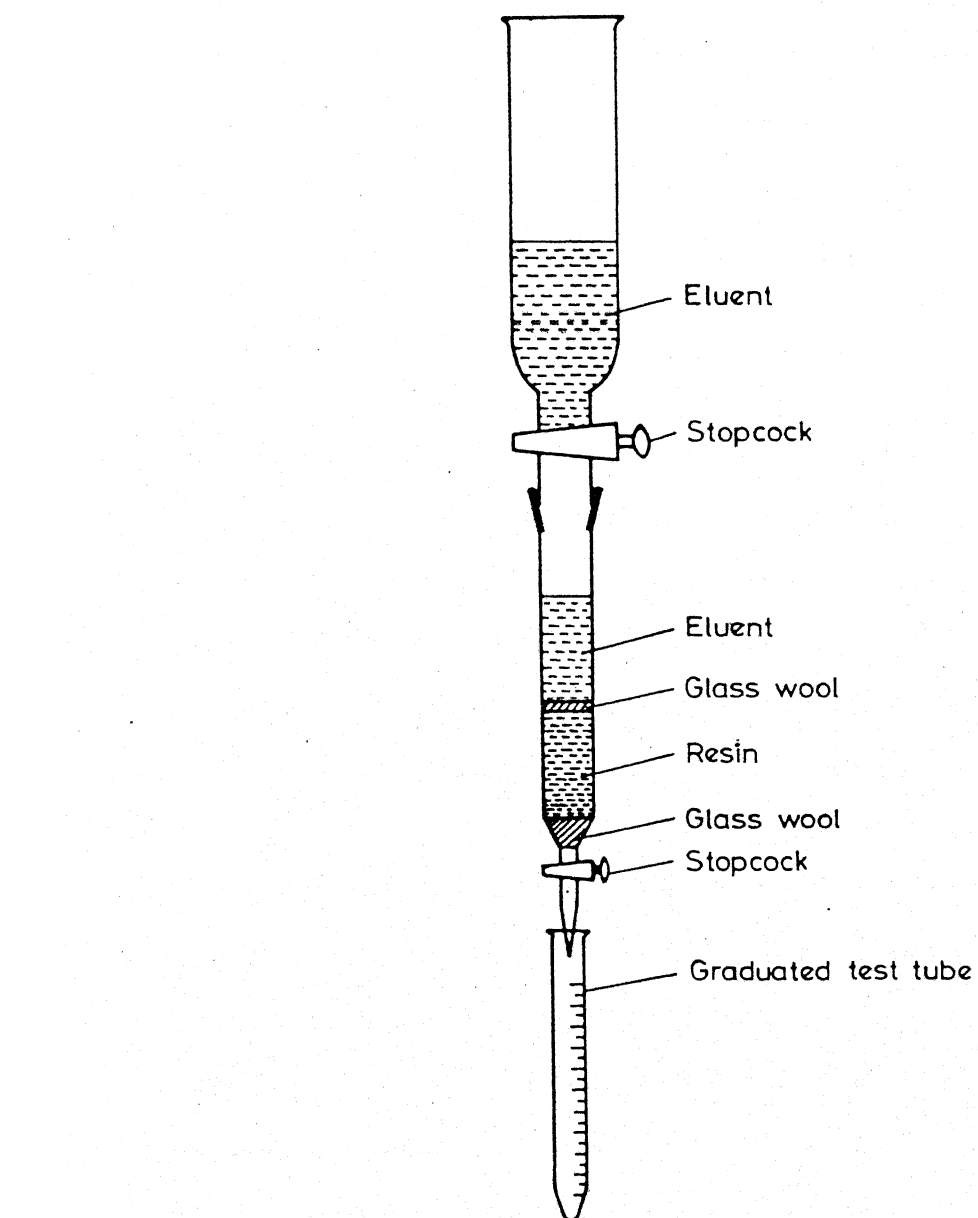


Fig.2-3-2 Set up of an ion exchange column.

2.3-5 Calibration of the Ion Exchange Column

Determination of the elution regions for CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ions:

0.1 ml of 0.1 M solution of the cation or the anion was first added to the top of the appropriate column using a graduated pipette or a hypodermic syringe and it was washed with distilled water. A small plug of glass wool was gently inserted from the top and the eluent was added. The column was then filled up with the eluent to a predetermined height to maintain the flow-rate of the eluate at 1 ml/min. The reservoir containing the eluent was attached to the column (Fig. 2.3-2). The stop-cock was then opened and successive 1 ml fractions of the effluent were collected in graduated and serially numbered test tubes. The following tests were carried out to detect the presence of the appropriate ions in these fractions.

Anions:

Two different procedures were used to detect the presence of an anion in an eluate fraction. (a) Chemical precipitation of the anion by treating with an appropriate reagent. The eluate volumes corresponding to the first and the last fractions at which the presence of the ion could be detected, were noted. The region between these

two points was taken as the elution region and the maximum of the peak was assumed to be situated at the middle of this region. (b) The relative amounts of the anion present in successive eluate fractions were determined spectrophotometrically. The plot of the absorbance vs. eluate volume gave the elution curve and the elution region.

The positions of the maximum of the anion by using methods (a) and (b) were found to agree well and so also the elution region.

Chromate Ion:

Eluted with 0.25 M NaNO_3 solution.

- (a) Each eluate fraction was treated with a few drops of 0.5N $\text{Pb}(\text{NO}_3)_2$ solution. The presence of chromate was indicated by the appearance of a yellow precipitate of PbCrO_4 .
- (b) The absorbance of each fraction was recorded at 371 nm. The plot of the absorbance vs. eluate volume is presented in the Fig. 2.3-3.

Dichromate Ion:

$\text{Cr}_2\text{O}_7^{2-}$ could not be eluted with 0.25M NaNO_3 solution or with more concentrated solutions up to 2M NaNO_3 . Therefore, the column was treated with 2-4 ml of 0.1M NaOH solution to convert $\text{Cr}_2\text{O}_7^{2-}$ into CrO_4^{2-} which could easily be eluted with

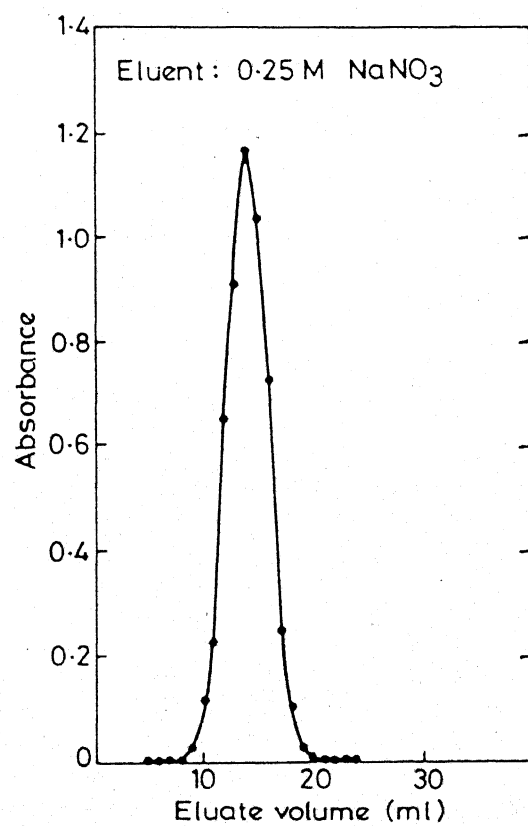


Fig. 2-3-3 Plot of absorbance vs eluate volume (ml) for CrO_4^{2-} at $\lambda=371\text{ nm}$.

0.25M NaNO_3 solution. For the detection of CrO_4^{2-} ions in the effluent, the same tests as above were carried out.

Details of the eluents and the elution regions for CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions are given in Table 2.3-3 below.

Table 2.3-3 : Elution Regions for Chromium Anions

Ion	Eluent/Conc.	Elution region (ml)	
		Method (a)	Method (b)
CrO_4^{2-}	0.25M NaNO_3	10-18	9-19
$\text{Cr}_2\text{O}_7^{2-}$	0.1M NaOH (4 ml)	-	-
	followed by 0.25M NaNO_3	10-18	9-19

When a mixture of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions were taken, the column was eluted first with 25 ml of 0.25M NaNO_3 . 4 ml of 0.1M NaOH was then added to convert the $\text{Cr}_2\text{O}_7^{2-}$ ions into CrO_4^{2-} ions and the latter was again eluted with another 25 ml of 0.25M NaNO_3 solution.

Cations:

Two different procedures were used to obtain the elution regions for different cationic species as mentioned in section 2.3-1.

(a) Elution regions and elution curves for $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ were obtained by spectrophotometric method. $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ were eluted with 0.5M HCl and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ was eluted with 2M HCl respectively. Absorbances were recorded at 287, 389 and 264 nm for $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ respectively. For each of these ions, a graph was plotted with absorbance vs. eluate volume. These are shown in Figures 2.3-4 and 2.3-5.

(b) Determination of elution regions and curves using radioactive $^{51}\text{Cr}(\text{III})$ solution in HCl:

The process of separation was the same as in (a). The concentration of a particular species in successive eluate fractions was determined by measuring the radioactivity of the fractions in a NaI(Tl) scintillation counter. Elution curves were obtained by plotting radioactivity vs. eluate volume for these species.

The details of the eluents and elution regions for $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ions are shown in Table 2.3-4.

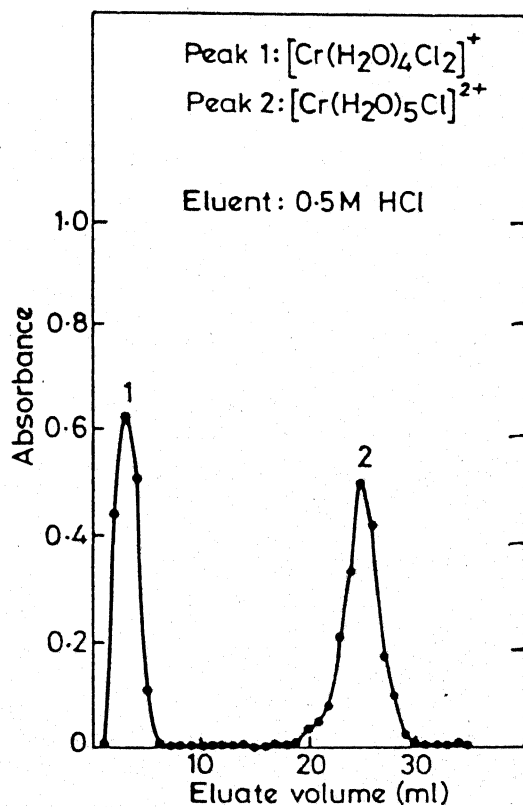


Fig. 2-3-4 Plot of absorbance vs eluate volume (ml) for $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ at $\lambda=287\text{ nm}$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ at $\lambda=389\text{ nm}$.

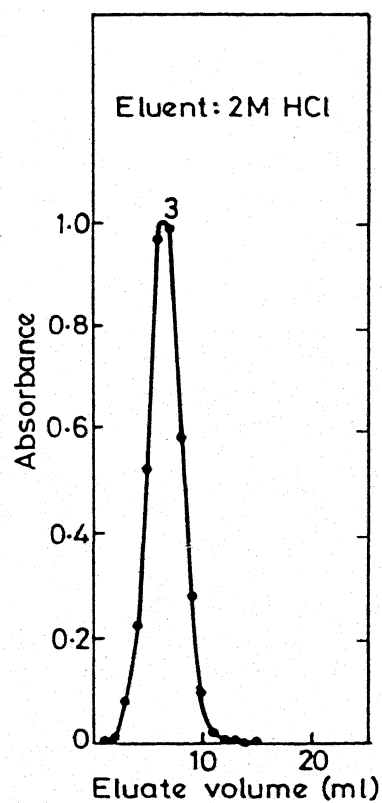


Fig. 2-3-5 Plot of absorbance vs eluate volume (ml) for $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ at $\lambda=264\text{ nm}$.

Table 2.3-4 : Elution Regions for Chromium Cations

Ion	Eluent/Conc.	Elution region (ml)	
		Method (a)	Method (b)
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$	0.5M HCl	1-6	1-6
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$	0.5M HCl	19-31	Absent
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	2.0M HCl	2-11	1-11

From the above table it is clear that the peak corresponding to $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ was not observed in a solution of radioactive $^{51}\text{Cr}(\text{III})$ in HCl. The other two peak positions obtained using the two methods agree well.

When a mixture of the three cations were taken, the column was eluted with 40 ml of 0.5M HCl and then with 40 ml of 2.0M HCl. For the radioactive sample of Cr^{3+} in HCl, eluted with 40 ml of each of 0.5M HCl and 2.0M HCl, a plot of radioactivity vs. eluate volume is given in Fig.2.3-6.

In one experiment using radioactive $^{51}\text{Cr}(\text{III})$ in HCl, the column was eluted with 40 ml of 0.5M HCl, 30 ml of 1.0M HCl and 30 ml of 2.0M HCl respectively. The object of this experiment was to check whether any other peak corresponding to some unknown species appear in the region eluted with 1.0M HCl. Figure 2.3-7 shows the plot of

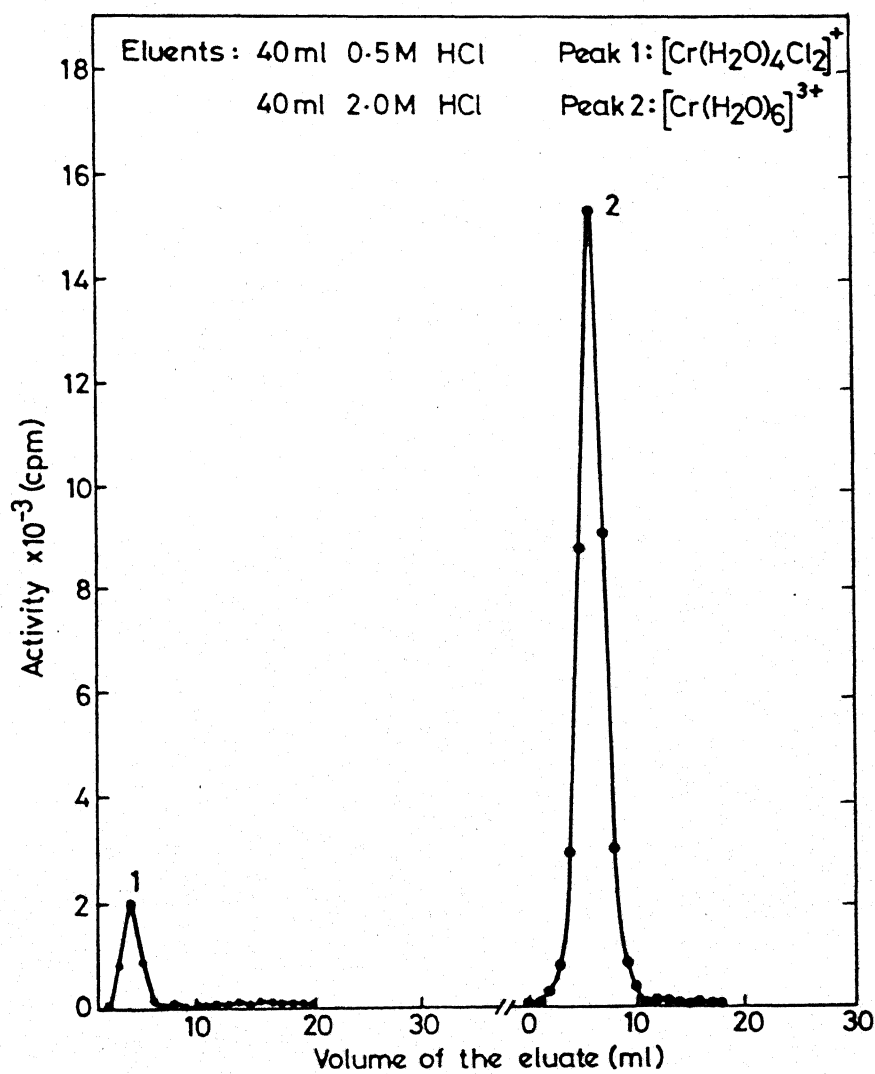


Fig.2-3-6 Plot of the activity vs volume of the eluate from cation exchange column for a solution of $^{51}\text{Cr}^{3+}$ in dilute HCl.

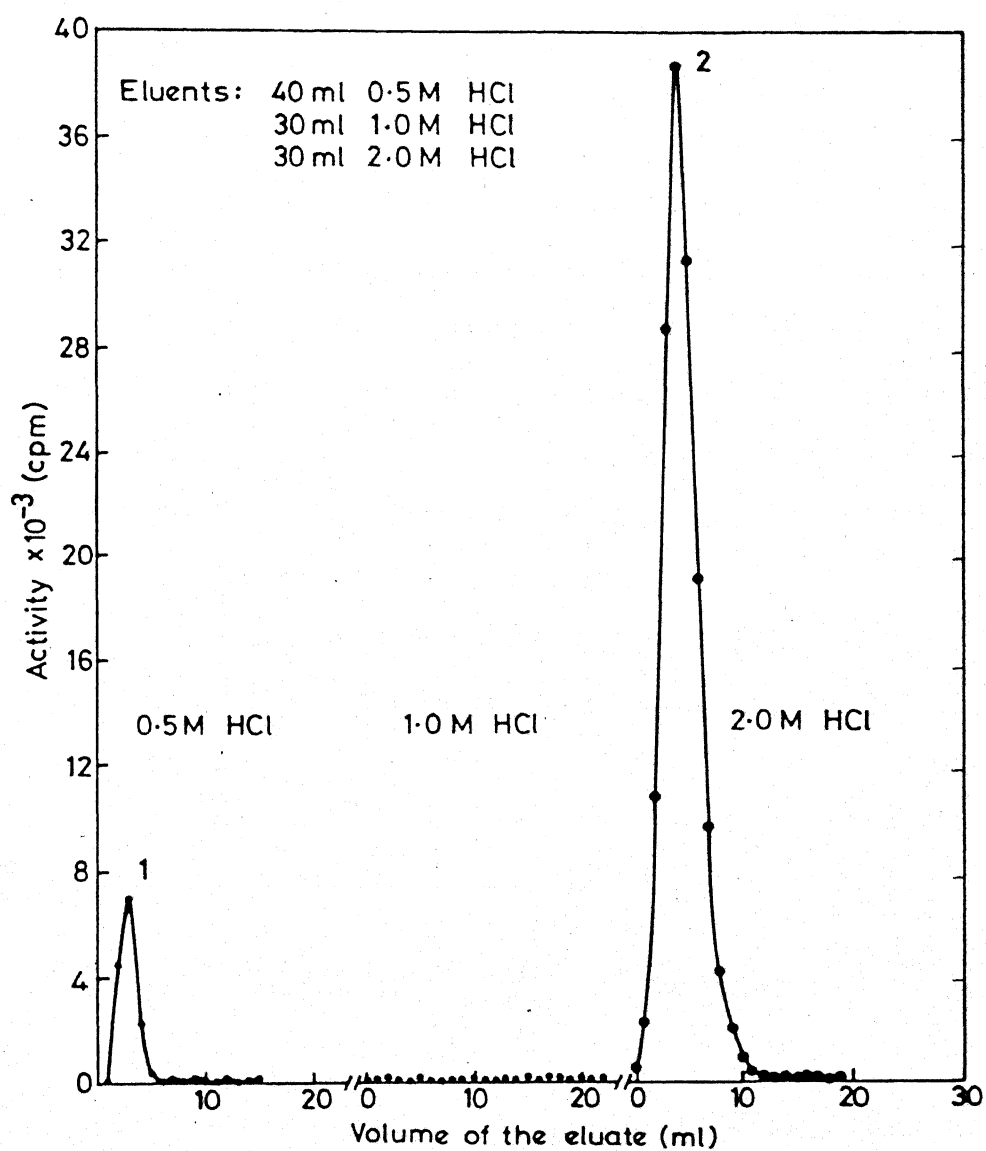


Fig.2-3-7 Plot of the activity vs volume of the eluate from cation exchange column for a solution of $^{51}\text{Cr}^{3+}$ in dilute HCl.

radioactivity vs. eluate volume for this experiment. The figure does not show the presence of any unknown species. Further, no residual activity was found in the resin after completion of the elution process.

Calibration with Ions in Acid Medium:

The salts were dissolved in 0.01N, 0.1N and 1 N H_2SO_4 in three different experiments. The elution regions were obtained following the same procedure as mentioned above. There was no change in the elution regions of any of the ions, except that with all concentrations of acid, CrO_4^{2-} was completely converted into $\text{Cr}_2\text{O}_7^{2-}$. Therefore, in all anion exchange separations, the column had to be treated with 2-4 ml of 0.1M NaOH solution before commencing elution with 0.25M NaNO_3 solution as described earlier.

Calibration of the Ion Exchange Column with Ions Using Dry DMF;

After the preparation of the ion exchange column 2 ml portions of dry DMF were made to pass through the column for about five times. Inactive $\text{Na}_2\text{Cr}_2\text{O}_7$ was dissolved in DMF and a small amount was adsorbed on the anion exchange column. The column was washed with distilled water and eluted with 4 ml of 0.1M NaOH followed by 25 ml of 0.25M NaNO_3 solution. The elution region for dichromate obtained was the same as that in the aqueous medium.

For different Cr(III) ions, the cation exchange column was prepared as described above. A solution of Cr(III) ions in distilled water (since the Cr(III)-complexes are insoluble in DMF) was added and eluted with 0.5M and 2.0M HCl solutions. Again the elution regions were found to be unchanged.

Effect of Time Gap between Adsorption and Elution of a Sample:

In the present investigation using TNI chromates and dichromates, it was observed that once a solution of the TNI salt was adsorbed on the cation exchange column, the elution pattern did not vary if eluted within about 5-6 hours. However, the eluted cationic activity increased with increasing time gap between the adsorption and the elution. Therefore, we have carried out all the elutions within 5 hours of adsorption. When, after a complete elution of the cation exchange column, it was left overnight with distilled water on it, on fresh elution with the same concentration of the eluent, some activity appeared in the eluate fractions. There was no such observation in the case of anion exchange column since all the activity was getting eluted with 0.1M NaOH and 0.25M NaNO_3 solutions and no residual activity was left in the resin. Some non-elutable activity (designated as Cr^{3+} dimer plus polymer) is always present on the cation exchanger which possibly breaks up into elutable Cr^{3+} (monomer) with time.

2.4 Ion Exchange Chromatographic Analysis of ^{51}Cr -ions from TNI K_2CrO_4 , Na_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Cr}_2\text{O}_7$ and Chromium Nitrate

2.4-1 General Procedure

A set of cation and anion exchange columns were prepared as described in section 2.3-4. The quartz ampoule

containing the irradiated salt was broken open. A portion ($\sim 5 - 10$ mg) of the content was dissolved in distilled water or in H_2SO_4 in presence or in absence of carrier(s) [CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$ and/or Cr^{3+}]. The quantity of chromate or dichromate carrier was very large compared to that of the TNI salt [$1\text{g}/2$ ml of Na_2CrO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7$ which corresponded to 160 mg/ml and 198 mg/ml of chromium respectively]. The only Cr(III) salt available was potassium chrome alum which could be used as a carrier. A maximum of ~ 500 mg of this salt could be dissolved in 2 ml of 1N H_2SO_4 which is equivalent to about 25 mg of Cr(III) per millilitre of the solution.

As soon as the TNI salt was added to the solution, a stop clock was started. A portion of the solution ($0.05 - 0.20$ ml) was drawn out using a graduated pipette or a hypodermic syringe (capacity - 0.25 ml) and added to the appropriate column at a time-interval t which was noted. The column was washed with distilled water and the washings were collected in graduated test tubes in 1 ml fractions till the last fraction was not radioactive. The column was then eluted with appropriate eluents. A series of separations were carried out at different noted time-intervals t .

2.4-2 Experiments in Nitrogen Atmosphere

The general procedure was the same as described in the preceding section. The samples were opened inside a

polyethylene glove-bag. The bag was flushed with nitrogen gas and all the solutions required for the experiment were also deaerated by bubbling nitrogen through them. After inserting all the materials inside, the opening of the bag was folded and closed with a clasp. The inflated bag was then maintained at a positive pressure of nitrogen. The following operations were performed inside the glove-bag: preparation of the ion exchange column, opening and dissolution of the sample, addition of the sample to the column, washing of the column with distilled water, and addition of the eluent to the column. After these steps the columns were taken out of the glove-bag and the rest of the experiment was carried out in open atmosphere as described in section 2.4-1.

2.4-3 Search for Neutral ^{51}Cr -activity in Solutions of Irradiated Chromates and Dichromates

A column of both anion and cation exchange resins was prepared in the following way. At first a 2 cm high anion exchange column was prepared and covered on top with a small piece of glasswool. A slurry of the cation exchange resin was poured on top of this upto another 2 cm height and again covered gently with glasswool. The column was then washed with distilled water to remove traces of H^+ and Cl^- ions from the resins.

0.1 ml of a fresh solution of TNI K_2CrO_4 in distilled water was added to the top of this column and, after adsorption, washed with distilled water. The effluent was collected in 1 ml fractions in graduated test tubes and their radioactivity measured. No activity could be detected in the washings indicating that no neutral form of ^{51}Cr is present in TNI K_2CrO_4 .

The above experiment was repeated with the following solutions: TNI K_2CrO_4 in 0.01N H_2SO_4 , TNI Na_2CrO_4 in distilled water and in 0.01N H_2SO_4 , TNI $K_2Cr_2O_7$ in distilled water and in 0.01N H_2SO_4 , and TNI $Na_2Cr_2O_7$ in distilled water, in 0.01N H_2SO_4 and in DMF. For the experiment in DMF, the column was pre-treated with dry DMF as described in section 2.3-5.

In all these experiments, no neutral ^{51}Cr -activity could be detected.

2.4-4 Experiments with TNI K_2CrO_4

General procedure was the same as described in section 2.4-1. The experiments were carried out under the following conditions. TNI K_2CrO_4 was dissolved in

- (i) distilled water in air,
- (ii) distilled water in nitrogen atmosphere,
- (iii) 0.01N H_2SO_4 without added carrier,
- (iv) 1.0N H_2SO_4 without added carrier,

- (v) 2 ml of 1N H_2SO_4 containing 1g of Na_2CrO_4 ,
- (vi) 2 ml of 1N H_2SO_4 containing 500 mg of potassium chrome alum, and
- (vii) 2 ml of 1N H_2SO_4 containing 1g of Na_2CrO_4 and 500 mg of potassium chrome alum.

In experiments (iii) - (vii), total anionic activity was determined by measuring the activity of the washings directly from the cation exchange columns. Cationic activity was separated as Cr(III)-monomer and Cr(III)-dimer and -polymer by eluting the column as described in section 2.3-5. Henceforth, Cr(III)-monomer will be designated as M and Cr(III)-dimer and -polymer, as DP.

Experiments in Distilled Water:

The TNI sample was dissolved in distilled water in absence of Cr(III)-carrier. The analytical procedure was same as given in section 2.4-1.

Analyses could not be carried out as a function of the time-interval in this case because the carrierless Cr(III)-activity was getting adsorbed on the glass walls of the test tubes. That the carrierless Cr(III)-activity in neutral solution was getting adsorbed on the glass walls was confirmed in the following way:

- (a) A small amount of TNI K_2CrO_4 was dissolved in distilled water. After a few minutes the solution was

transferred to another test tube and the activity of the first one was measured after rinsing with water. There was a considerable amount of activity in the empty test tube which could only be extracted by warming with a dilute acid.

(b) A solution of TNI K_2CrO_4 was made to pass through an anion exchange column, the washings (containing only cation) were collected and allowed to stand for 10 minutes. It was observed that all the radioactivity got adsorbed on the glass walls.

(c) A solution of TNI K_2CrO_4 was passed through a cation exchange column. The column was washed with 5 ml of distilled water and the washings (containing only anion) were collected and left undisturbed for 10 minutes in glass test tubes. At the end of this period, the solution from each test tube was removed and it was rinsed with water and on measuring gave counts equal to the background counts indicating that the anionic activity (which was not carrierless) was not getting adsorbed on glass.

(d) A small amount of TNI K_2CrO_4 was dissolved in water in presence of a few milligrams of potassium chrome alum. A portion of it was passed through an anion exchange column. The column was washed with distilled water and the washings were allowed to stand for 10 minutes. The solution was then transferred to another test tube and the activity of the empty test tube was measured after rinsing it with

distilled water. The observed counts corresponded to the background counts indicating that $^{51}\text{Cr}(\text{III})$ -activity in the presence of $\text{Cr}(\text{III})$ -carrier was not getting adsorbed on glass.

All these experiments show that only carrierless $^{51}\text{Cr}(\text{III})$ -activity was getting adsorbed on the glass walls of the test tubes. Similar results were observed with other TNI chromates and dichromates under investigation.

In all subsequent experiments, therefore, TNI salts were dissolved in sulphuric acid. In the experiments where the solution was first passed through cation exchange column, the column was washed with distilled water. But, when the solution was first passed through an anion exchange column, it was necessary to wash the column with 0.05 N HCl to extract all the cationic activity, which otherwise (with water) was forming insoluble $\text{Cr}(\text{OH})_3$ and it was impossible to wash this out of the anion exchange column with water.

Experiment in Distilled Water in Nitrogen Atmosphere:

This experiment was performed inside a glove-bag filled with nitrogen gas. The procedure is described in section 2.4-2.

Only one experiment was performed under this condition. An ampoule containing TNI K_2CrO_4 was broken

open and the whole content was transferred to the top of the cation exchange column. Distilled water was added to it and four minutes passed before the whole solution was adsorbed on the resin. The column was then washed with distilled water and the washings were directly passed through an anion exchange column. Elution of the columns were carried out following the procedure described in section 2.3-5.

Although the TNI salt was K_2CrO_4 , after eluting with 25 ml of 0.25M $NaNO_3$ solution, it was found that an intense orange coloured band was not eluted out. This band was due to the conversion of CrO_4^{2-} to $Cr_2O_7^{2-}$ in presence of H^+ ions displaced from the column by K^+ ions. The column was treated with 4 ml of 0.1N NaOH solution, which converted this into a yellow band which was then eluted out with 0.25M $NaNO_3$ solution as CrO_4^{2-} .

Results of all the above experiments are presented in section 3.1 of Chapter III.

2.4-5 Experiments with TNI Na_2CrO_4

The following experiments were performed with TNI Na_2CrO_4 . TNI Na_2CrO_4 was dissolved in

- (i) distilled water in air,
- (ii) 0.01N H_2SO_4 without added carrier,
- (iii) 1N H_2SO_4 without added carrier,

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- (iv) 2 ml of 1N H_2SO_4 containing 1g of Na_2CrO_4 ,
- (v) 2 ml of 1N H_2SO_4 containing 500 mg of potassium chrome alum, and
- (vi) 2 ml of 1N H_2SO_4 containing 1g of Na_2CrO_4 and 500 mg of potassium chrome alum.

Experiment (i) was performed at only one time interval and experiments (ii) - (vi) were time-based experiments. Results of all these experiments are given in section 3.2 of Chapter III.

2.4-6 Experiments with TNI $\text{K}_2\text{Cr}_2\text{O}_7$

With TNI $\text{K}_2\text{Cr}_2\text{O}_7$, experiments were carried out by dissolving the salt in

- (i) distilled water,
- (ii) 0.1N HCl ,
- (iii) 0.1N HNO_3 ,
- (iv) 0.01N H_2SO_4 ,
- (v) 0.1N H_2SO_4 ,
- (vi) 1.0N H_2SO_4 ,
- (vii) 2 ml of 1N H_2SO_4 containing 1g of $\text{Na}_2\text{Cr}_2\text{O}_7$
- (viii) 2 ml of 1N H_2SO_4 containing 500 mg of potassium chrome alum,
- (ix) 2 ml of 1N H_2SO_4 containing 1g of $\text{Na}_2\text{Cr}_2\text{O}_7$ and 500 mg of potassium chrome alum,
- (x) 1N H_2SO_4 maintained at a temperature of $0 \pm 1^\circ\text{C}$, and
- (xi) 1N H_2SO_4 maintained at a temperature of $90 \pm 1^\circ\text{C}$.

Experiments (i) and (ii) were carried out at only one time interval whereas (iii) - (xi) were time-based experiments. The results are shown in Chapter III, (section 3.3).

2.4-7 Experiments with TNI $\text{Na}_2\text{Cr}_2\text{O}_7$

With TNI $\text{Na}_2\text{Cr}_2\text{O}_7$, experiments were performed under the following conditions. TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ was dissolved in

- (i) distilled water,
- (ii) DMF in a nitrogen atmosphere,
- (iii) DMF in air,
- (iv) 0.01N H_2SO_4 ,
- (v) 1.0N H_2SO_4 ,
- (vi) 2 ml of 1N H_2SO_4 containing 1g of $\text{Na}_2\text{Cr}_2\text{O}_7$,
- (vii) 2 ml of 1N H_2SO_4 , containing 500 mg of potassium chrome alum, and
- (viii) 2 ml of 1N H_2SO_4 containing 1g of $\text{Na}_2\text{Cr}_2\text{O}_7$ and 500 mg of potassium chrome alum.

The results of all these experiments are presented in section 3.4 of Chapter III as time based data. Experiment (i) was performed only at one time interval owing to the difficulty mentioned in section 2.4-4.

Details of the Experiments with TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ in DMF:

These experiments were carried out in order to study the effect of a non-aqueous solvent on the irradiated salt.

The ion exchange column was prepared in the same manner as described in section 2.3-4 and then treated with small portions of dry DMF. TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ was dissolved in DMF and aliquots from this solution were added to cation exchange columns at different time-intervals. After adsorption of the solution on the column, it was washed with distilled water and elution was done following the same procedure as in all other experiments.

For the experiment in DMF in a nitrogen atmosphere, all the steps upto the addition of the eluent to the column were carried out in a glove-bag containing nitrogen gas.

2.4-8 Experiments with TNI Chromium Nitrate

The procedure followed in the analysis of TNI chromium nitrate was the same as that for a TNI chromate or a dichromate. The solution was always passed through a cation exchange column and the effluent from this was directly added to the top of an anion exchange column. This arrangement was necessary because it was found that a certain fraction of ^{51}Cr -activity was not retained by either the cation or anion exchange column. This form of activity was assumed to be a neutral ^{51}Cr -species. The final washings from the second column (anion exchange) of the series were collected in graduated and serially numbered test tubes. The anion and the cation exchange

columns were eluted using appropriate eluents.

Specific Conditions and the Details of the Experiments:

(i) In Distilled Water:

A small amount of TNI $\text{Cr}(\text{NO}_3)_3$ was dissolved in 2 ml of distilled water and two aliquots of 0.25 ml each were added to two sets of cation and anion exchange columns at $t = 2$ minutes and $t = 20$ minutes respectively. The rest of the procedure was same as described previously. Results are shown in Table 3.5-1.

(ii) In 1N H_2SO_4 :

The same steps as in (i) were repeated with the sample dissolved in 1N H_2SO_4 . The experiment was carried out at $t = 2$ minutes only. Percentage activities of various species are given in Table 3.5-2.

(iii) In Alkaline Medium in Presence of $^{51}\text{CrO}_4^{2-}$ Ion:

A portion of pure $^{51}\text{Cr}(\text{III})$ -monomer (obtained from an experiment using TNI K_2CrO_4) was oxidized to $^{51}\text{CrO}_4^{2-}$ on boiling with excess of NaOH solution and H_2O_2 . Excess H_2O_2 was removed by prolonged boiling and the solution was evaporated to dryness. Distilled water was then added to make the volume upto 1 ml and its activity was measured. About 3 mg of TNI $\text{Cr}(\text{NO}_3)_3$ from a fresh ampoule was then dissolved in this solution and

the whole amount was added to the top of a cation exchange column the effluent from which was directly passed to the top of an anion exchange column. The same procedure as in other experiments was then followed. The results are presented in Table 3.5-3.

- (iv) In 1N H_2SO_4 containing mg quantity of Cr^{6+} - carrier:

A small amount of TNI $\text{Cr}(\text{NO}_3)_3$ was dissolved in 2 ml of 1N H_2SO_4 containing 10 mg of Na_2CrO_4 and aliquots were analyzed at $t = 1.5, 15$ and 180 minutes in the usual manner. Results are given in Table 3.5-4.

- (v) In 1N H_2SO_4 containing large excess of Cr^{6+} -carrier:

TNI $\text{Cr}(\text{NO}_3)_3$ was dissolved in 2 ml of 1N H_2SO_4 containing an excess of Na_2CrO_4 (1g/2 ml) and aliquots from this were analyzed at $t = 1.5, 15, 30$ and 60 minutes. Results of this experiment are presented in Table 3.5-5.

- (vi) Experiment with TNI $\text{Cr}(\text{NO}_3)_3$ dissolved in 1N H_2SO_4 to which TNI K_2CrO_4 was added after 2 minutes:

A small amount of TNI $\text{Cr}(\text{NO}_3)_3$ was dissolved in 0.5 ml of 1N H_2SO_4 . 0.05 ml of this solution was taken out in a test tube and its radioactivity was measured. The volume of the remaining 0.45 ml of the solution was made up to 2 ml with 1N H_2SO_4 . After 2 minutes (measured from the instant of dissolution of $\text{Cr}(\text{NO}_3)_3$), a small

amount of $\text{TNI K}_2\text{CrO}_4$ was added to this. An aliquot of 0.15 ml from this was added to a cation exchange column after 2 minutes of dissolution of $\text{TNI K}_2\text{CrO}_4$. The rest of the procedure was the same as in case of other experiments using $\text{TNI Cr}(\text{NO}_3)_3$. This experiment was repeated at $t = 10$ minutes.

A 0.15 ml portion of the solution was taken in a separate test tube to determine the total activity of the mixture from which the activity due to $\text{TNI K}_2\text{CrO}_4$ could be estimated.

The results of this experiment are shown in Table 3.5-6.

The significance of all these results and their probable interpretations will be discussed in Chapter IV.

2.5 Detection and Measurement of γ -Radiation (61-66)

All the radioactivity measurements were done using a NaI(Tl) scintillation detector connected to other accessories of the counting assembly. The principle of radiation detection and the counting assembly used in the present work are discussed in the following sections.

2.5-1 Interaction of Radiation with Matter

When a charged particle like an alpha or a beta particle passes through matter, it loses its energy by Coulomb interaction with the electrons of the surrounding

medium. Such interactions result in the excitation and ionization of the atoms or molecules of the surrounding medium. This ionization and/or excitation is the basis of operation of all major detectors for charged particles. Gamma radiation also interacts with matter in a similar way and results in exciting and ionizing the molecules of the matter traversed.

For detection of a particular type of radiation, the choice of the detector depends mainly on the manner in which that radiation interacts with matter. Gamma rays lose energy by three fundamental processes while traversing through a medium. These are photoelectric effect, Compton scattering and pair production.

(i) Photoelectric Effect:

In this process, an incoming photon of energy $h\nu$ ejects an electron from an atom or a molecule and imparts to it an energy E_e given by

$$E_e = h\nu - E_b$$

where E_b is the binding energy of the electron. If this is an inner-shell electron (e.g. K-shell) of an atom, then the vacancy so created is filled by another electron from an upper shell (e.g. L-shell) thus emitting a characteristic X-ray. In a fraction of the cases, these X-rays produce secondary emission of electrons called Auger electrons.

For photon energies well above the K-binding energy of the absorber, the photoelectric absorption first falls off rapidly (about as $E_{\gamma}^{-7/2}$), then more slowly (eventually as E_{γ}^{-1}) with increasing energy. It is also proportional to Z^5 . Photoelectric process is the predominant mode of interaction for γ -rays (or X-rays) of low energy.

(ii) Compton Scattering:

Instead of giving up its entire energy to a bound electron, a photon appears to transfer only a part of its energy to an electron. The photon appears not only degraded in energy but also deflected from its original path. This effect is called Compton scattering. The relation between the energy loss and the scattering angle θ can be derived from the relativistic conditions of conservation of momentum and energy and it takes the form

$$h\nu' = \frac{h\nu}{1 + \frac{h\nu}{m_0 c^2} (1 - \cos\theta)}$$

where $h\nu$ is the incident photon energy, $h\nu'$ is the scattered photon energy and $m_0 c^2$, the rest mass energy of an electron.

The scattering cross-section per atom is proportional to Z . For energies in excess of 0.5 MeV it is approximately proportional to E_{γ}^{-1} . Thus, Compton scattering falls off much more slowly with increasing energy than photoelectric absorption

upto 2 MeV.

(iii) Pair Production:

If the γ -energy exceeds twice the rest mass energy of an electron ($2m_0c^2 = 1.02 \text{ MeV}$) the process of pair production is energetically possible. In this interaction, a γ -ray photon disappears and is replaced by an electron-positron pair. All the energy carried by the photon above 1.02 MeV goes into the kinetic energy shared by the positron and the electron. After slowing down in the medium, the positron is subsequently annihilated producing two photons as secondary interaction products. The cross-section for pair-production first increases slowly with increase in γ -energy and above 4 MeV becomes proportional to Z^2 .

Since the atomic cross-sections for all these processes discussed increase with increasing Z , heavy elements are very effective absorbers of electromagnetic radiation.

2.5-2 The Scintillation Process

The absorption of energy by a substance and its re-emission as visible and near-visible radiation are known as luminescence. The scintillation process accompanying any nuclear radiation has its origin in the

our experiments, a well-type detector (SH 644W) manufactured by the Electronic Corporation of India Limited (ECIL) has been used. Exactly equal volumes of the effluent from the ion exchange columns were taken in the test tubes of identical shape and size for counting activities. This was necessary since counting efficiency depends on the geometry of the sample inside the well-type detector.

Approximately 30 eV of energy deposition in a NaI(Tl) crystal is required to produce one light photon and it takes, on an average, about 10 photons to release one photoelectron at the photocathode of the multiplier. These photoelectrons are then accelerated by a potential of the order of 100V to the first dynode where each one produces n secondary electrons. These secondary electrons are similarly accelerated and multiplied n -fold at the second dynode and so on. With 10 dynodes and with n typically about 3-4, the total multiplication factor is n^{10} or of the order of 10^5 to 10^6 . Thus, a 0.3 MeV γ -ray absorbed in a NaI(Tl) crystal might produce 10^4 light photons giving 10^3 primary photoelectron leading to an output pulse of about 0.16V requiring only a modest amplification in a pulse amplifier.

The output pulse from the photomultiplier is fed into a linear amplifier (PA 521, ECIL). The output from the amplifier is passed through a discriminator (SC 6046, ECIL)

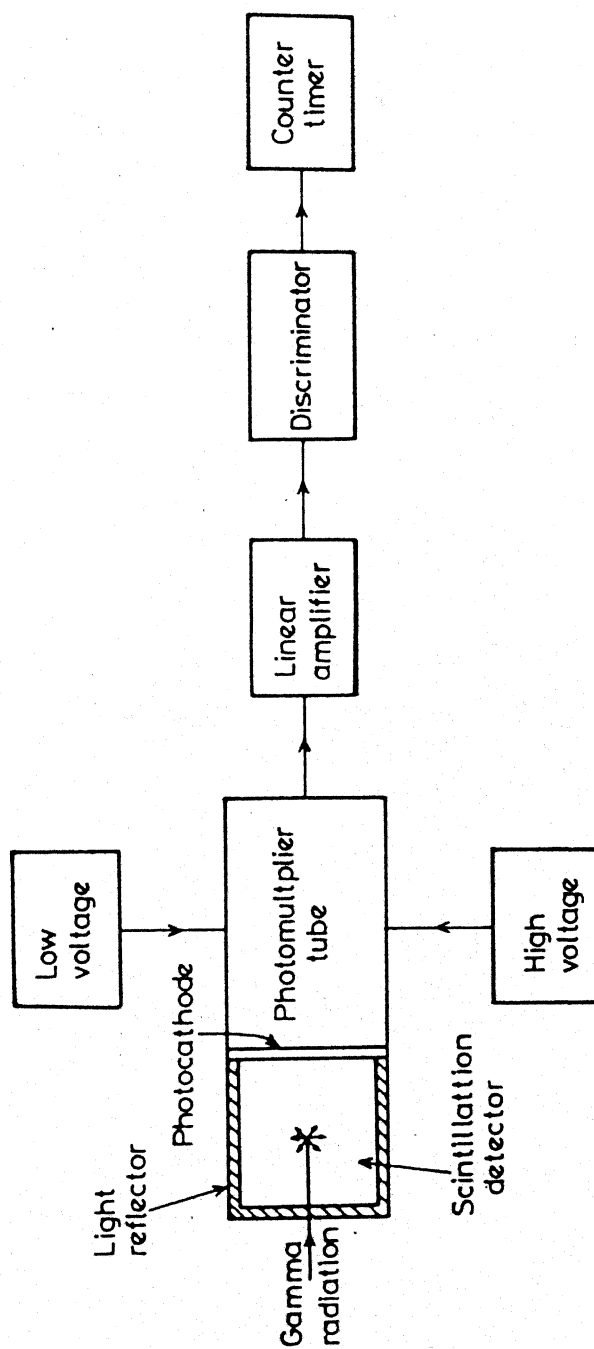


Fig. 2.5-1 Block diagram of the scintillation counting assembly.

into a display unit (EC 5104, ECIL). A high voltage unit of the type HV 4826A, manufactured by ECIL, has been used. A block diagram of the counting assembly is shown in Fig. 2.5-1.

The detector was placed inside a lead castle which could be opened from the top for placing the sample inside. The test tube containing the sample was placed inside the well making sure that the part of the test tube containing the liquid was inside the well and was surrounded by the detector.

CHAPTER III

RESULTS

3.1 Results of the Experiments with TNI K_2CrO_4

This section presents the results of the experiments carried out with TNI K_2CrO_4 under different conditions. Tables 3.1-1 and 3.1-2 show the results of the analyses of TNI K_2CrO_4 when dissolved in distilled water in the presence of air and in a nitrogen atmosphere respectively. Figures 3.1-1(a) and (b) are the elution curves for TNI K_2CrO_4 obtained by plotting the activity of a collected fraction against the eluate volume at which the fraction was collected. Tables 3.1-3 - 3.1-7 and Figures 3.1-2 - 3.1-6 show the percentage activities of Cr(VI), Cr(III)-monomer (M) and Cr(III)-dimer and polymer (DP) for TNI K_2CrO_4 corresponding to different time-intervals t . All the results are the mean values of duplicate measurements, along with the standard deviations, unless otherwise stated. Table 3.1-1 shows a typical result of duplicate experiments as an illustration.

In all the plots of percentage activity vs. time-interval, the size of each point is such that it includes the deviation from the mean and therefore, it was not necessary to indicate the error bars.

Table 3.1-1 : Percentage activities of Cr(VI), M and DP for TNI K_2CrO_4 dissolved in distilled water in presence of air at $t = 2$ minutes. Duplicate results are shown along with the deviation from the mean.

Set No.	Cr(VI) (%)	M(%)	DP(%)
I	68.32	16.70	14.98
II	69.46	16.28	14.26
Mean	68.89 \pm 0.57	16.49 \pm 0.21	14.62 \pm 0.36

Table 3.1-2 : Percentage activities* of Cr(VI), M and DP for TNI K_2CrO_4 dissolved in distilled water in a nitrogen atmosphere at $t = 2$ minutes.

Cr(VI) [CrO_4^{2-}] (%)	Cr(VI) [$Cr_2O_7^{2-}$] (%)	M(%)	DP(%)
14.04	53.10	16.50	16.36

* Results of single measurements.

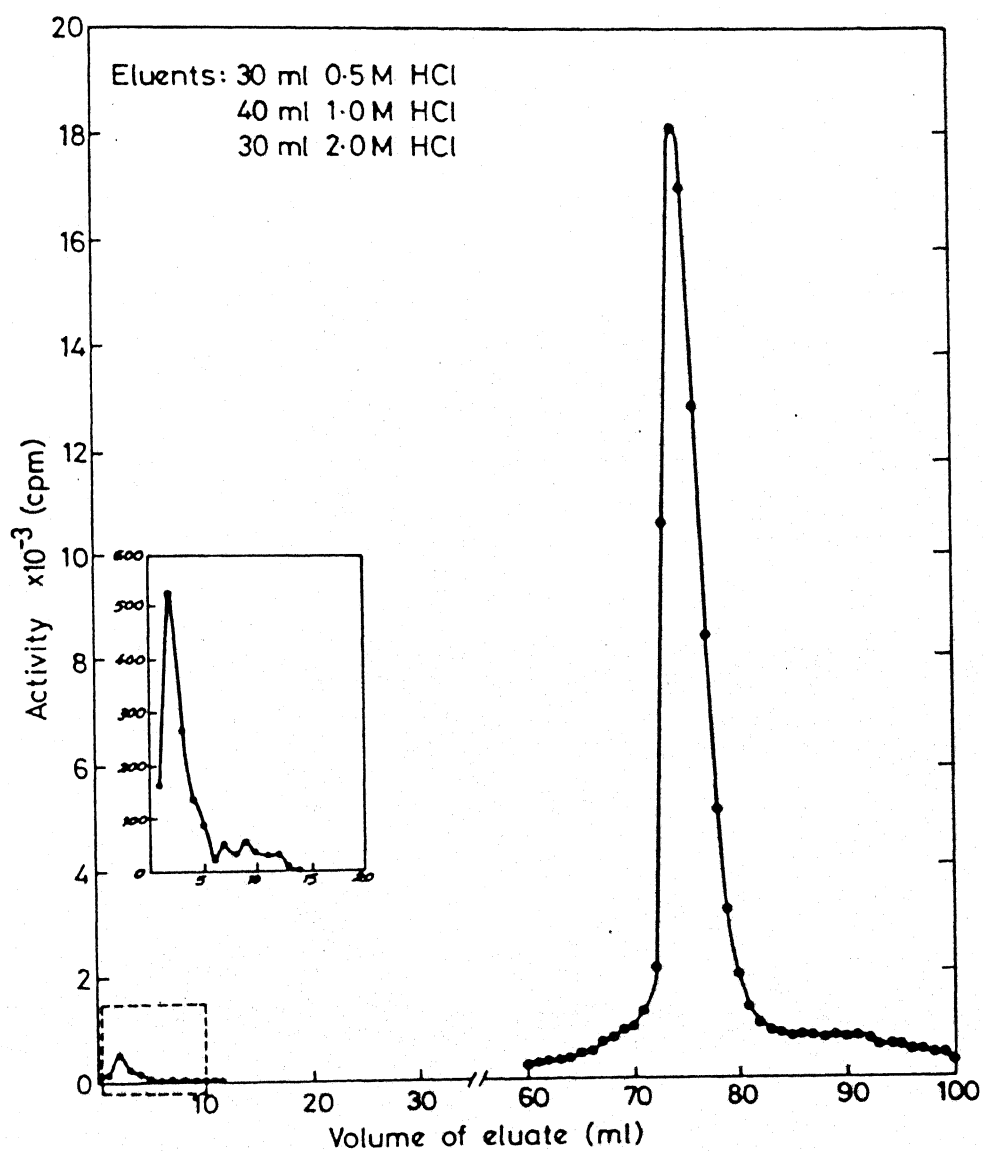


Fig 3-1-1a Plot of activity vs volume of eluate of the cation exchange column for TNI K_2CrO_4 dissolved in distilled water under nitrogen atmosphere. Inset: enlarged plot for the first peak.

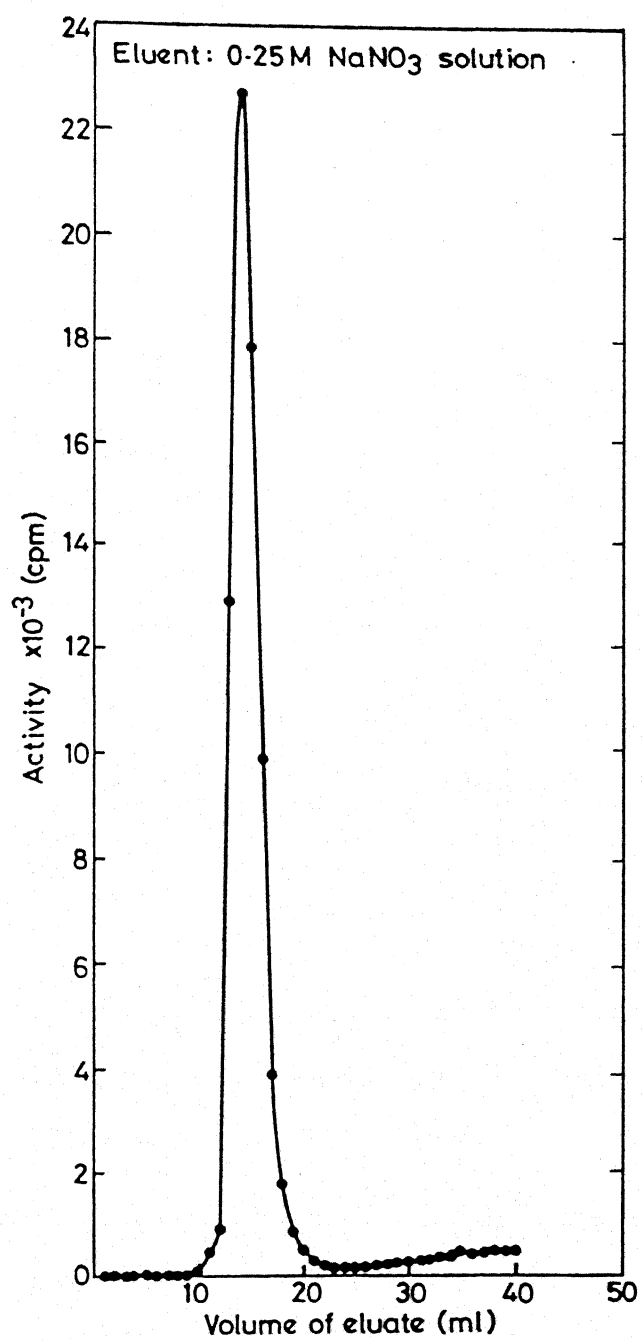


Fig.3-1-1b Plot of activity vs volume of eluate of the anion exchange column for TNI K₂CrO₄ dissolved in distilled water under nitrogen atmosphere.

Table 3.1-3 : Percentage activities of Cr(VI), M and DP for TNI K_2CrO_4 dissolved in 0.01N H_2SO_4 as a function of the time-interval t.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	53.20 \pm 0.80	32.62 \pm 0.62	14.18 \pm 0.18
5	53.04 \pm 0.32	32.50 \pm 0.26	14.46 \pm 0.06
16	52.50 \pm 0.23	33.39 \pm 0.12	14.11 \pm 0.11
35	49.72 \pm 0.29	37.52 \pm 0.18	12.76 \pm 0.11
50	48.76 \pm 0.06	40.41 \pm 0.05	10.83 \pm 0.01
65	50.17 \pm 0.52	41.38 \pm 0.36	8.45 \pm 0.16

Table 3.1-4 : Percentage activities of Cr(VI), M and DP for TNI K_2CrO_4 dissolved in 1N H_2SO_4 as a function of the time-interval t.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	58.28 \pm 0.45	29.73 \pm 0.14	11.99 \pm 0.31
5	55.44 \pm 0.43	33.72 \pm 0.24	10.48 \pm 0.19
16	53.64 \pm 0.29	37.53 \pm 0.14	8.83 \pm 0.15
30	51.57 \pm 0.29	41.40 \pm 0.18	7.03 \pm 0.11
45	51.87 \pm 0.51	41.61 \pm 0.30	6.52 \pm 0.21
60	51.76 \pm 0.23	42.01 \pm 0.08	6.23 \pm 0.15

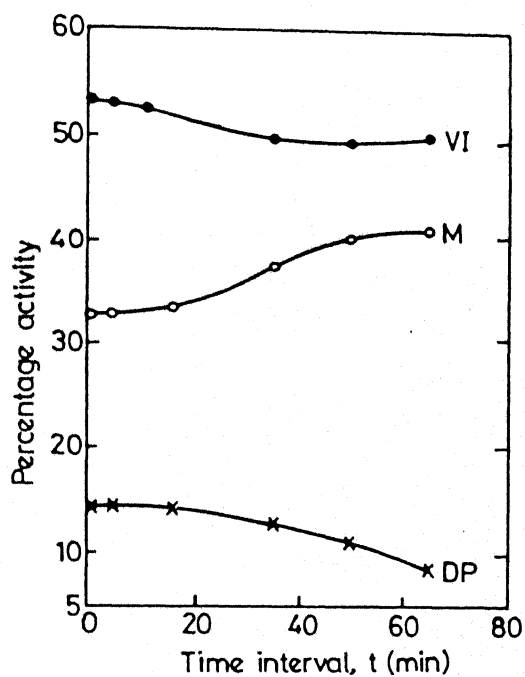


Fig. 3-1-2 Plot of percentage activity vs t for a solution of TNI K_2CrO_4 in 0.01N H_2SO_4 .

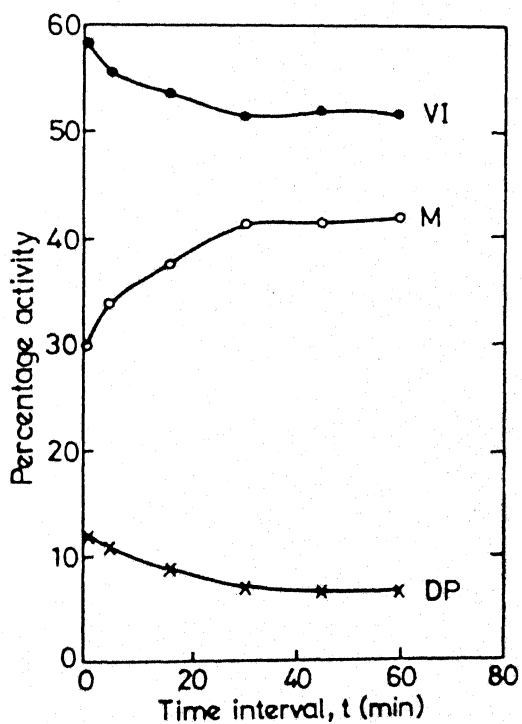


Fig. 3-1-3 Plot of percentage activity vs t for a solution of TNI K_2CrO_4 in 1N H_2SO_4 .

Table 3.1-5 : Percentage activities of Cr(VI), M and DP for TNI K_2CrO_4 dissolved in 2 ml of 1N H_2SO_4 containing 1g of inactive Na_2CrO_4 as a function of the time-interval t.

t(min)	Cr (VI) (%)	M(%)	DP (%)
1	67.49 \pm 0.37	18.60 \pm 0.25	13.91 \pm 0.12
5	67.70 \pm 0.38	19.06 \pm 0.33	13.24 \pm 0.05
15	68.13 \pm 0.43	20.75 \pm 0.22	11.12 \pm 0.21
30	67.24 \pm 0.23	24.68 \pm 0.05	8.08 \pm 0.18
45	68.15 \pm 0.33	24.39 \pm 0.29	7.46 \pm 0.04
60	68.63 \pm 0.31	23.64 \pm 0.16	7.73 \pm 0.15

Table 3.1-6 : Percentage activities of Cr(VI), M and DP for TNI K_2CrO_4 dissolved in 2ml of 1N H_2SO_4 containing 500 mg of potassium chrome alum as a function of the time-interval t.

t(min)	Cr (VI) (%)	M(%)	DP (%)
1	53.64 \pm 0.28	22.88 \pm 0.21	23.48 \pm 0.07
5	51.80 \pm 0.55	25.57 \pm 0.24	22.63 \pm 0.31
15	48.45 \pm 0.51	31.89 \pm 0.40	19.66 \pm 0.11
30	48.83 \pm 0.39	35.69 \pm 0.14	15.48 \pm 0.25
45	49.77 \pm 0.29	35.72 \pm 0.25	14.51 \pm 0.04
60	49.53 \pm 0.44	35.54 \pm 0.28	14.93 \pm 0.16

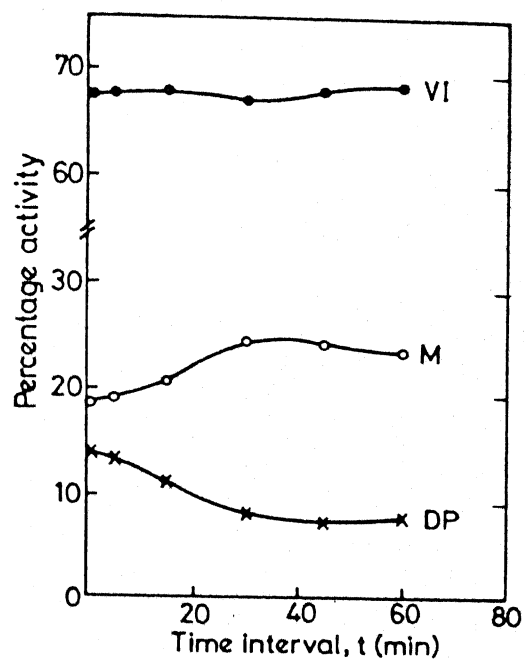


Fig. 3-1-4 Plot of percentage activity vs t for TNI K_2CrO_4 in a solution of 1N H_2SO_4 and excess of CrO_4^{2-} carrier.

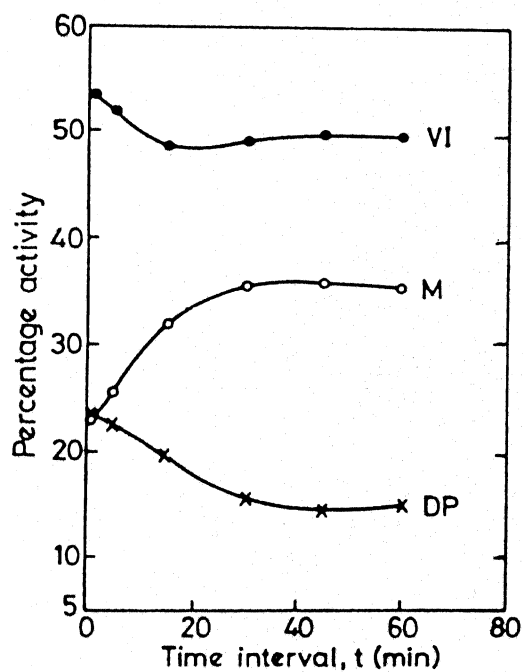


Fig 3-1-5 Plot of percentage activity vs t for TNI K_2CrO_4 in a solution of 1N H_2SO_4 and excess of Cr^{3+} carrier.

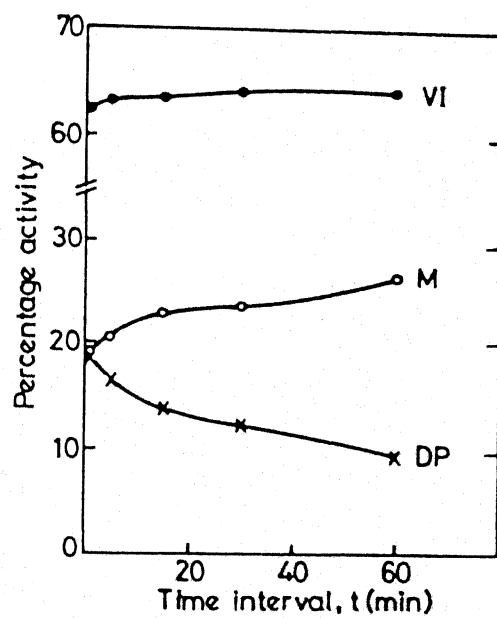


Fig.3-1-6 Plot of percentage activity vs t for TNI K_2CrO_4 in a solution of 1N H_2SO_4 and excess of both CrO_4^{2-} and Cr^{3+} carriers.

Table 3.1-7 : Percentage activities of Cr(VI), M and DP for TNI K_2CrO_4 dissolved in 2 ml of 1N H_2SO_4 containing 1g of Na_2CrO_4 and 500 mg of potassium chrome alum as a function of the time-interval t .

t(min)	Cr(VI) (%)	M (%)	DP (%)
1	62.41 \pm 0.35	19.14 \pm 0.30	18.45 \pm 0.05
5	63.29 \pm 0.38	20.36 \pm 0.22	16.35 \pm 0.16
15	63.52 \pm 0.46	22.80 \pm 0.24	13.68 \pm 0.22
30	64.19 \pm 0.50	23.64 \pm 0.21	12.16 \pm 0.29
60	64.21 \pm 0.43	26.57 \pm 0.35	9.22 \pm 0.08

3.2 Results of the Experiments with TNI Na_2CrO_4

This section presents the results of the experiments carried out with TNI Na_2CrO_4 . Table 3.2-1 shows percentage activities of the various ^{51}Cr -species when TNI Na_2CrO_4 is dissolved in distilled water. Tables 3.2-2 - 3.2-6 and Figures 3.2-1 - 3.2-5 present the time based data for the system under a variety of conditions specifically stated.

Table 3.2-1 : Percentage activities of Cr(VI), M and DP for TNI Na_2CrO_4 dissolved in distilled water in air at $t = 2$ minutes.

Cr(VI) (%)	M(%)	DP(%)
71.46 ± 0.72	23.69 ± 0.23	4.85 ± 0.49

Table 3.2-2 : Percentage activities of Cr(VI), M and DP for TNI Na_2CrO_4 dissolved in 0.01N H_2SO_4 as a function of the time-interval t .

$t(\text{min})$	Cr(VI) (%)	M(%)	DP(%)
1	68.10 ± 0.46	23.80 ± 0.15	8.10 ± 0.31
5	69.16 ± 0.54	23.49 ± 0.39	7.35 ± 0.15
20	68.10 ± 0.35	23.44 ± 0.20	8.46 ± 0.15
40	68.75 ± 0.18	23.30 ± 0.06	7.95 ± 0.12
60	69.10 ± 0.14	24.15 ± 0.11	6.75 ± 0.03

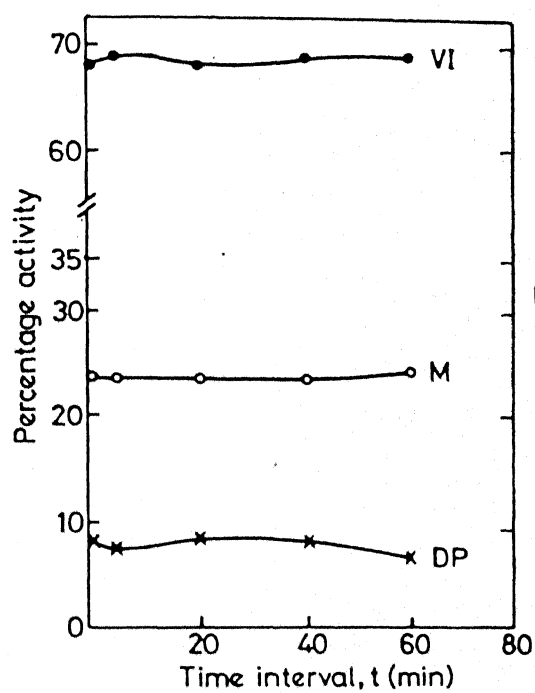


Fig. 3.2-1 Plot of percentage activity vs t for TNI Na_2CrO_4 in $0.01\text{N H}_2\text{SO}_4$.

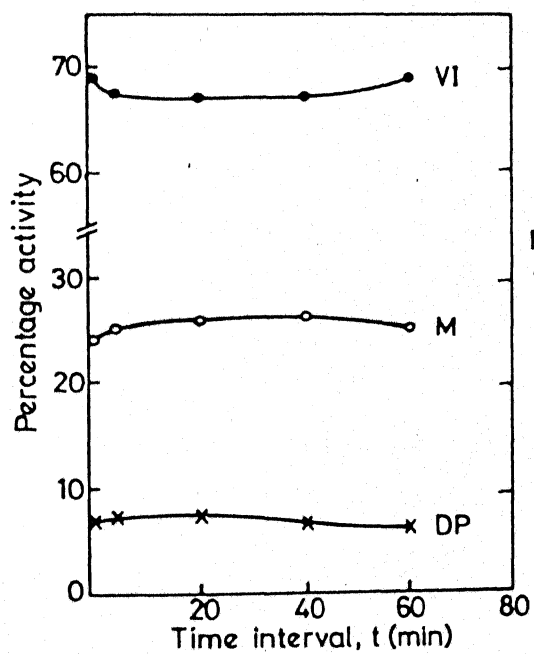


Fig. 3.2-2 Plot of percentage activity vs t for TNI Na_2CrO_4 in $1\text{N H}_2\text{SO}_4$.

Table 3.2-3 : Percentage activities of Cr(VI), M and DP for TNI Na_2CrO_4 dissolved in 1N H_2SO_4 as a function of the time-interval t .

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	69.05 \pm 0.20	24.03 \pm 0.12	6.92 \pm 0.08
5	67.57 \pm 0.19	25.17 \pm 0.12	7.26 \pm 0.07
20	67.11 \pm 0.68	25.78 \pm 0.39	7.11 \pm 0.29
40	67.25 \pm 0.59	26.12 \pm 0.24	6.63 \pm 0.35
60	69.08 \pm 0.73	24.94 \pm 0.25	5.98 \pm 0.48

Table 3.2-4 : Percentage activities of Cr(VI), M and DP for TNI Na_2CrO_4 dissolved in 1N H_2SO_4 containing 1g of inactive Na_2CrO_4 as a function of the time-interval t .

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	71.21 \pm 0.48	22.65 \pm 0.29	6.14 \pm 0.19
5	70.95 \pm 0.34	23.22 \pm 0.16	5.83 \pm 0.18
20	71.40 \pm 0.52	23.71 \pm 0.33	4.89 \pm 0.19
40	71.42 \pm 0.28	23.95 \pm 0.11	4.63 \pm 0.17
60	71.22 \pm 0.31	24.42 \pm 0.21	4.36 \pm 0.10

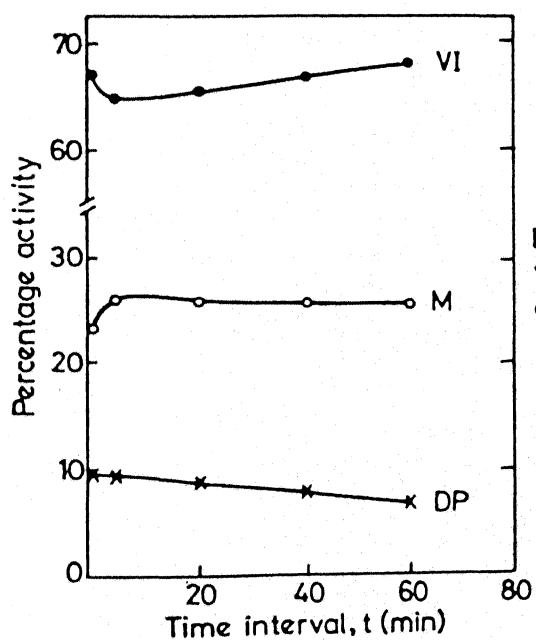
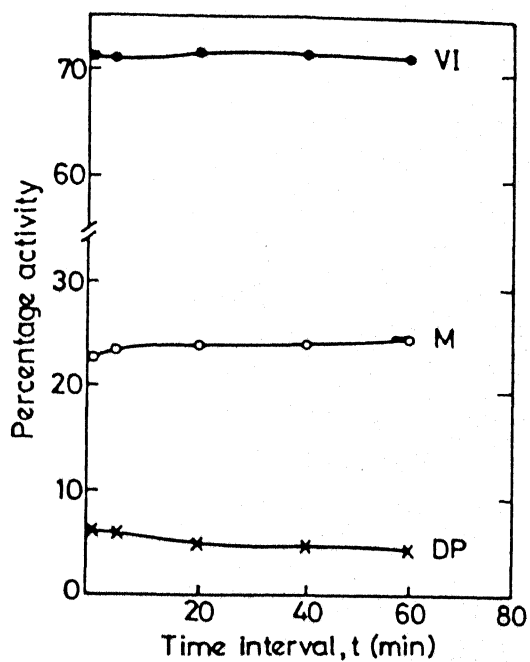


Table 3.2-5 : Percentage activities of Cr(VI), M and DP for TNI Na_2CrO_4 dissolved in 2 ml of 1N H_2SO_4 containing 500 mg of potassium chrome alum as a function of the time-interval t.

t(min)	Cr(VI) (%)	M(%)	DP (%)
1	67.14 \pm 0.66	23.25 \pm 0.49	9.61 \pm 0.17
5	64.80 \pm 0.59	25.99 \pm 0.32	9.21 \pm 0.27
20	65.56 \pm 0.61	25.78 \pm 0.28	8.66 \pm 0.33
40	66.77 \pm 0.38	25.57 \pm 0.31	7.66 \pm 0.07
60	68.22 \pm 0.42	25.29 \pm 0.15	6.49 \pm 0.27

Table 3.2-6 : Percentage activities of Cr(VI), M and DP for TNI Na_2CrO_4 dissolved in 2 ml of 1N H_2SO_4 containing 1g of Na_2CrO_4 and 500 mg of potassium chrome alum as a function of the time-interval t.

t(min)	Cr(VI) (%)	M(%)	DP (%)
1	69.48 \pm 0.37	22.49 \pm 0.26	8.03 \pm 0.11
5	69.69 \pm 0.43	22.83 \pm 0.38	7.48 \pm 0.05
20	70.76 \pm 0.16	22.75 \pm 0.08	6.49 \pm 0.08
40	71.02 \pm 0.51	23.22 \pm 0.27	5.76 \pm 0.24
60	70.91 \pm 0.35	23.99 \pm 0.18	5.10 \pm 0.17

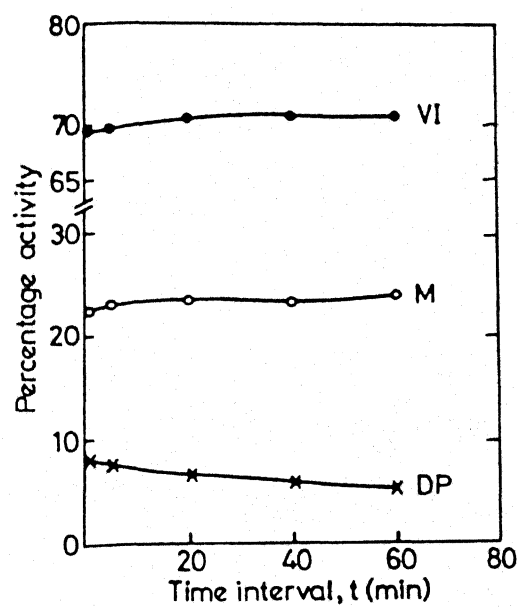


Fig. 3-2-5 Plot of percentage activity vs t for TNI Na_2CrO_4 in a solution of excess of both CrO_4^{2-} & Cr^{3+} carriers in 1N H_2SO_4 .

3.3 Results of the Experiments with TNI $K_2Cr_2O_7$

The results of the experiments performed with TNI $K_2Cr_2O_7$ under various conditions are presented in tables 3.3-1 - 3.3-7 of this section. Figures 3.3-1 - 3.3-7 show the time based data in the form of plots of percentage yield against the time-interval t .

Table 3.3-1 : Percentage activities of Cr(VI), M and DP for TNI $K_2Cr_2O_7$ dissolved in distilled water in air at $t = 2$ minutes.

Cr(VI) (%)	M (%)	DP (%)
89.02 \pm 0.79	5.73 \pm 0.44	5.25 \pm 0.35

Table 3.3-2 : Percentage activities of Cr(VI), M and DP for TNI $K_2Cr_2O_7$ dissolved in different acids of 0.1N - strength corresponding to the stated time-intervals t .

Acid	t (min)	Cr(VI) (%)	M (%)	DP (%)
0.1N HCl	1.5	84.16 \pm 0.51	8.86 \pm 0.09	6.98 \pm 0.42
0.1N HNO_3	1.5	82.53 \pm 0.44	9.44 \pm 0.16	8.03 \pm 0.28
	10	78.08 \pm 0.19	13.28 \pm 0.12	8.64 \pm 0.07
	30	83.05 \pm 0.22	9.70 \pm 0.11	7.25 \pm 0.11
	7260	82.62 \pm 0.63	15.43 \pm 0.46	1.95 \pm 0.17

Continued....

Table 3.3-2 (Continued):

Acid	t (min)	Cr (VI) (%)	M (%)	DP (%)
0.1N H ₂ SO ₄	1	85.64±0.37	7.47±0.21	6.89±0.15
	5	86.08±0.43	7.77±0.28	6.15±0.15
	16	84.24±0.19	10.27±0.08	5.49±0.11
	35	85.70±0.29	9.74±0.13	4.56±0.16
	60	87.35±0.47	8.98±0.31	3.67±0.16

Table 3.3-3 : Percentage activities of Cr(VI), M and DP for TNI K₂Cr₂O₇ dissolved in 0.01N H₂SO₄ as a function of the time interval t.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	85.65±0.28	7.46±0.21	6.89±0.07
5	86.48±0.20	7.27±0.17	6.25±0.03
16	84.34±0.27	10.27±0.16	5.39±0.11
35	85.33±0.19	10.44±0.11	4.23±0.08
60	86.49±0.18	10.50±0.09	3.01±0.09

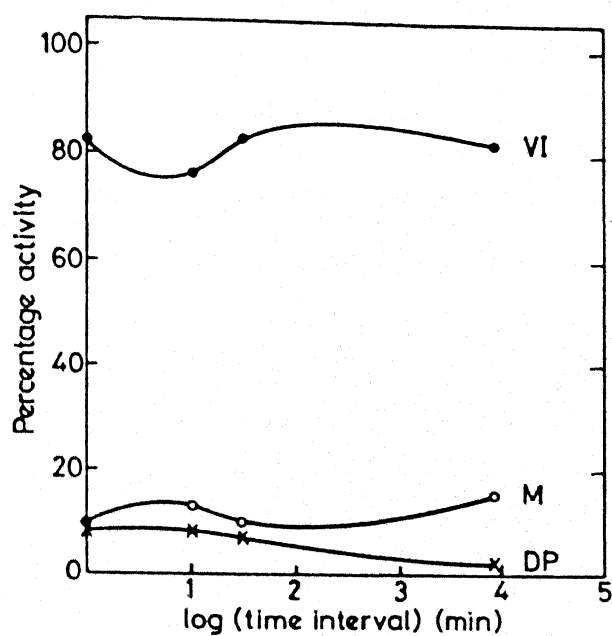


Fig. 3-3-1 Plot of percentage activity vs log (time interval) for TNI $K_2Cr_2O_7$ in 0.1N HNO_3 .

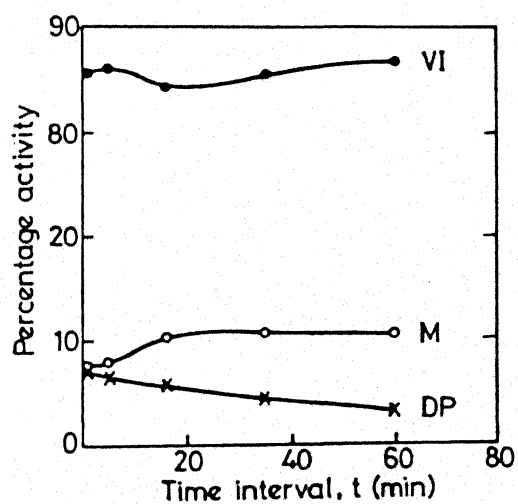


Fig. 3-3-2 Plot of percentage activity vs t for TNI $K_2Cr_2O_7$ in 0.01N H_2SO_4 .

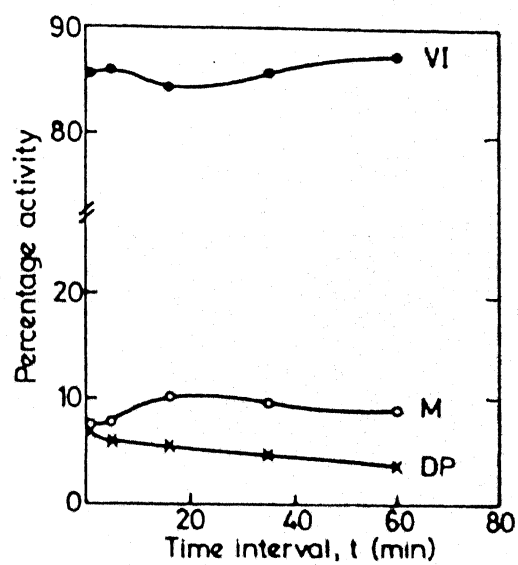


Fig. 3-3-3 Plot of percentage activity vs t for TNI $K_2Cr_2O_7$ in 0.1N H_2SO_4 .

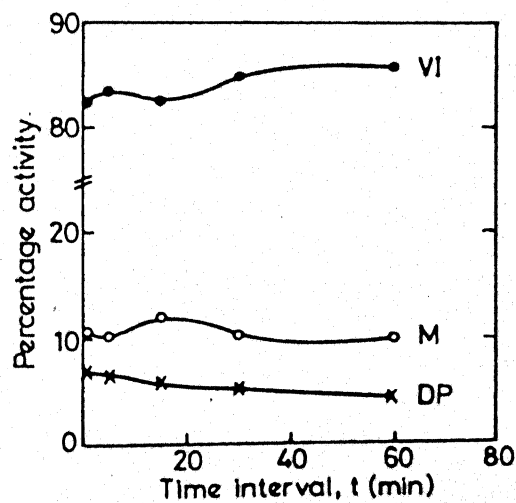


Fig. 3-3-4 Plot of percentage activity vs t for TNI $K_2Cr_2O_7$ in 1N H_2SO_4 .

Table 3.3-4 : Percentage activities of Cr(VI), M and DP for TNI $K_2Cr_2O_7$ dissolved in 1N H_2SO_4 as a function of the time-interval t.

t(min)	Cr(VI) (%)	M (%)	DP (%)
1	82.39 \pm 0.33	10.79 \pm 0.30	6.83 \pm 0.03
5	83.44 \pm 0.38	10.19 \pm 0.37	6.38 \pm 0.01
15	82.41 \pm 0.37	11.91 \pm 0.33	5.68 \pm 0.04
30	84.80 \pm 0.07	10.11 \pm 0.02	5.11 \pm 0.05
60	85.71 \pm 0.32	9.87 \pm 0.31	4.43 \pm 0.01

Table 3.3-5 : Percentage activities of Cr(VI), M and DP for TNI $K_2Cr_2O_7$ dissolved in 2 ml of 1N H_2SO_4 containing 1g of $Na_2Cr_2O_7$ as a function of the time-interval t.

t(min)	Cr(VI) (%)	M (%)	DP (%)
1	88.78 \pm 0.20	6.02 \pm 0.19	5.20 \pm 0.01
6	88.33 \pm 0.34	7.22 \pm 0.29	4.45 \pm 0.13
16	88.13 \pm 0.29	8.44 \pm 0.27	3.43 \pm 0.02
40	88.89 \pm 0.07	8.22 \pm 0.05	2.89 \pm 0.02
60	88.03 \pm 0.41	8.70 \pm 0.32	3.27 \pm 0.09
2880	88.10 \pm 0.04	9.22 \pm 0.02	2.68 \pm 0.02

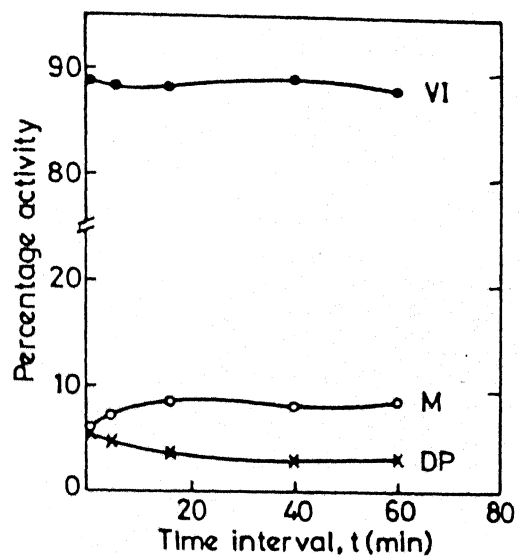


Fig. 3-3-5 Plot of percentage activity vs t for Tl $K_2Cr_2O_7$ in 1N H_2SO_4 in presence of excess of $Cr_2O_7^{2-}$ carrier.

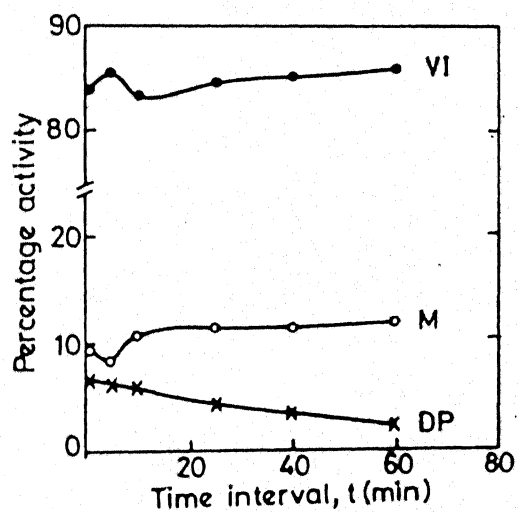


Fig. 3-3-6 Plot of percentage activity vs t for Tl $K_2Cr_2O_7$ dissolved in 1N H_2SO_4 in presence of excess of Cr^{3+} carriers.

Table 3.3-6 : Percentage activities of Cr(VI), M and DP for TNI $K_2Cr_2O_7$ dissolved in 2 ml of 1N H_2SO_4 containing 500 mg of potassium chrome alum as a function of the time-interval t.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	84.04 \pm 0.28	9.38 \pm 0.21	6.58 \pm 0.07
5	85.64 \pm 0.23	8.32 \pm 0.17	6.04 \pm 0.06
10	83.30 \pm 0.22	10.85 \pm 0.14	5.85 \pm 0.08
25	84.44 \pm 0.25	11.37 \pm 0.23	4.19 \pm 0.02
40	85.14 \pm 0.18	11.52 \pm 0.17	3.34 \pm 0.01
60	85.86 \pm 0.02	11.92 \pm 0.01	2.22 \pm 0.01

Table 3.3-7 : Percentage activities of Cr(VI), M and DP for TNI $K_2Cr_2O_7$ dissolved in 2 ml of 1N H_2SO_4 containing 1g of inactive $Na_2Cr_2O_7$ and 500 mg of potassium chrome alum as a function of the time-interval t.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	87.15 \pm 0.34	6.86 \pm 0.22	5.99 \pm 0.12
10	87.78 \pm 0.15	7.55 \pm 0.11	4.67 \pm 0.04
20	87.89 \pm 0.21	8.09 \pm 0.14	4.02 \pm 0.07
30	88.99 \pm 0.23	7.90 \pm 0.18	3.11 \pm 0.05
45	89.06 \pm 0.30	7.85 \pm 0.21	3.09 \pm 0.09
65	89.40 \pm 0.09	8.02 \pm 0.08	2.58 \pm 0.01

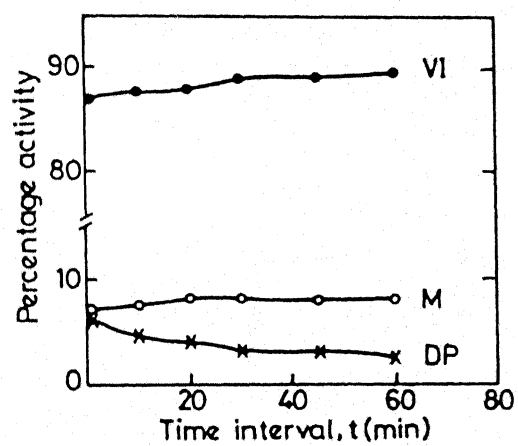


Fig. 3-3-7 Plot of percentage activity vs t for $\text{TNl K}_2\text{Cr}_2\text{O}_7$ dissolved in $1\text{N H}_2\text{SO}_4$ in presence of excess of both $\text{Cr}_2\text{O}_7^{2-}$ and Cr^{3+} carriers.

Tables 3.3-8 and 3.3-9 present the relative yields of Cr(VI), M and DP for TNI $K_2Cr_2O_7$ dissolved in 1N H_2SO_4 corresponding to two different temperatures ($0^\circ C$ and $90^\circ C$).

Figures 3.3-8a and 3.3-8b are the plots of the same data.

Table 3.3-8 : Percentage activities* of Cr(VI), M and DP for TNI $K_2Cr_2O_7$ dissolved in 1N H_2SO_4 at $0^\circ C$ and maintained at $0 \pm 1^\circ C$ for one hour.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	86.74	6.75	6.15
5	86.35	8.89	4.76
15	87.90	6.93	5.17
35	88.57	6.44	4.99
60	87.50	7.18	5.32

* Results of single measurements.

Table 3.3-9 : Percentage activities* of Cr(VI), M and DP for TNI $K_2Cr_2O_7$ dissolved in 1N H_2SO_4 at $90^\circ C$ and maintained at $90 \pm 1^\circ C$ for one hour.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	86.66	8.51	4.83
4	88.97	9.92	1.11
15	88.20	10.98	0.82
35	86.11	12.98	0.91
60	87.85	11.48	0.67

* Results of single measurements.

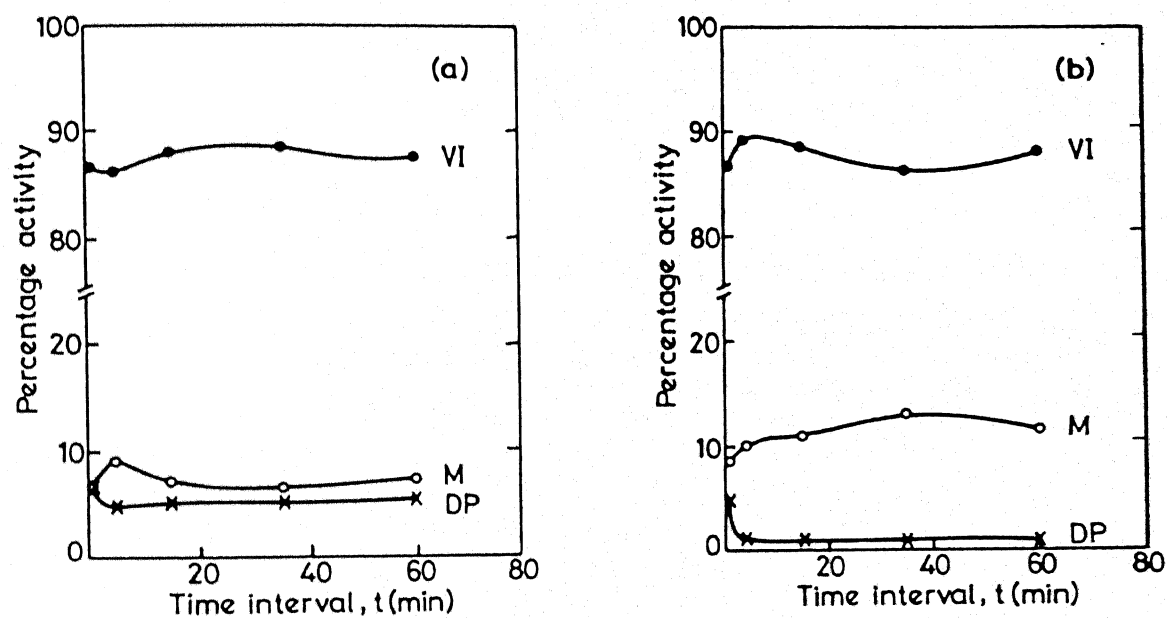


Fig.3-3-8 Plot of percentage activity vs t for TNi $\text{K}_2\text{Cr}_2\text{O}_7$ dissolved in 1N H_2SO_4 : (a) at $0 \pm 1^\circ\text{C}$ and (b) at $90 \pm 1^\circ\text{C}$.

3.4 Results of the Experiments with TNI $\text{Na}_2\text{Cr}_2\text{O}_7$

This section presents the results of the experiments with TNI $\text{Na}_2\text{Cr}_2\text{O}_7$. Tables 3.4-1, 3.4-2 and 3.4-3 are the results of the analyses of TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ in distilled water in air, in DMF in a nitrogen atmosphere and in DMF in air, respectively. Figure 3.4-1 is the plot of the percentage activities of Cr(VI), M and DP against the time-interval t for the data shown in Table 3.4-3. Tables 3.4-4 - 3.4-9 show the time based data for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ under different stated conditions which are also shown as plots of percentage activity vs. the time-interval in Figures 3.4-2 - 3.4-7 respectively.

Table 3.4-1 : Percentage activities of Cr(VI), M and DP for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ dissolved in distilled water in air at $t = 1$ minute .

Cr(VI) (%)	M (%)	DP (%)
82.74 \pm 0.75	10.50 \pm 0.70	6.76 \pm 0.05

Table 3.4-2 : Percentage activities* of Cr(VI), M and DP for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ dissolved in DMF in a nitrogen atmosphere as a function of the time-interval t.

t(min)	Cr(VI) (%)	M (%)	DP (%)
2	90.74	2.17	7.09
10	90.17	2.35	7.48
25	90.57	2.41	7.02

* Results of single measurements.

Table 3.4-3 : Percentage activities* of Cr(VI), M and DP for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ dissolved in DMF in air as a function of the time-interval t.

t(min)	Cr(VI) (%)	M (%)	DP (%)
1.5	86.16	5.27	8.54
3	86.73	5.18	8.09
15	86.41	5.63	7.96
30	86.49	5.75	7.76
60	86.12	6.57	7.31

* Results of single measurements.

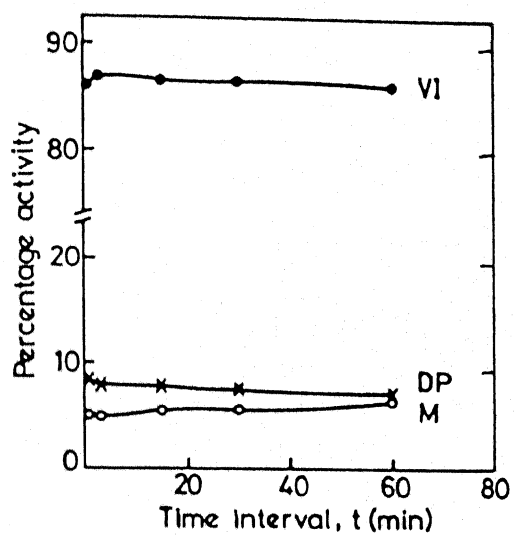


Fig. 3-4-1 Plot of percentage activity vs t for TNi $\text{Na}_2\text{Cr}_2\text{O}_7$ dissolved in dry DMF in air.

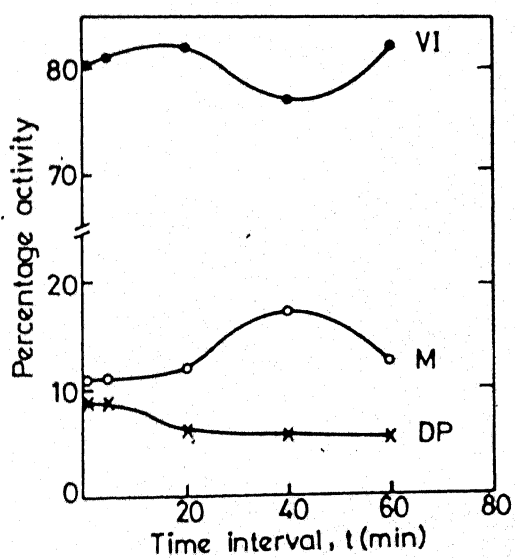


Fig. 3-4-2 Plot of percentage activity vs t for TNi $\text{Na}_2\text{Cr}_2\text{O}_7$ in 0.01N H_2SO_4 .

Table 3.4-4 : Percentage activities of Cr(VI), M and DP for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ in 0.01N H_2SO_4 as a function of the time-interval t.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	80.54 \pm 0.51	10.83 \pm 0.19	8.63 \pm 0.32
5	81.02 \pm 0.34	11.16 \pm 0.28	7.82 \pm 0.06
20	81.94 \pm 0.52	12.02 \pm 0.27	6.04 \pm 0.25
40	76.97 \pm 0.29	17.27 \pm 0.12	5.76 \pm 0.17
60	82.24 \pm 0.31	12.56 \pm 0.08	5.20 \pm 0.23

Table 3.4-5 : Percentage activities of Cr(VI), M and DP for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ in 1N H_2SO_4 as a function of the time-interval t.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	76.18 \pm 0.44	12.71 \pm 0.23	11.11 \pm 0.21
5	77.92 \pm 0.56	15.42 \pm 0.29	6.66 \pm 0.27
20	77.86 \pm 0.19	16.26 \pm 0.09	5.88 \pm 0.10
40	74.62 \pm 0.28	19.52 \pm 0.15	5.86 \pm 0.13
60	78.51 \pm 0.32	15.57 \pm 0.12	5.92 \pm 0.20

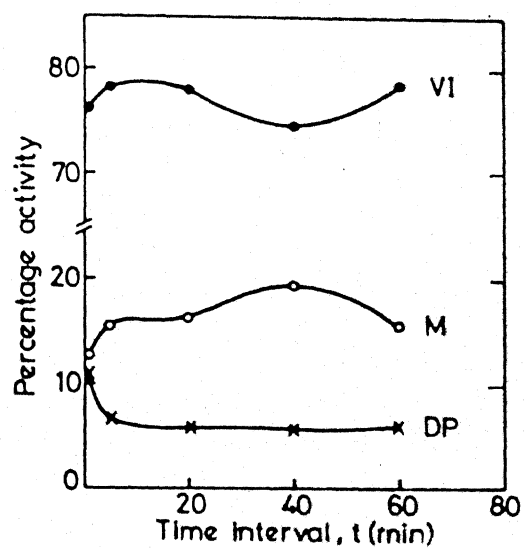


Fig. 3-4-3 Plot of percentage activity vs t for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ in 1N H_2SO_4

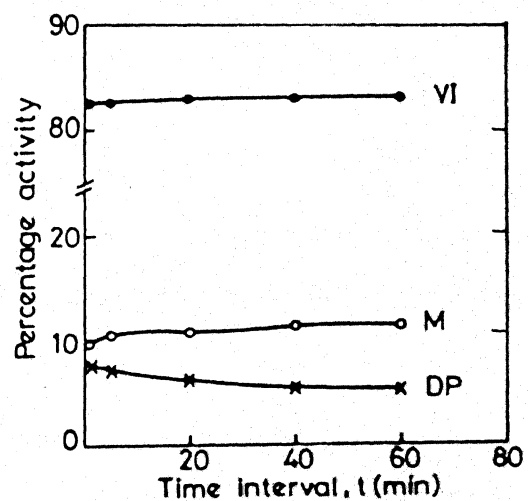


Fig. 3-4-4 Plot of percentage activity vs t for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ dissolved in 1N H_2SO_4 in presence of excess of $\text{Cr}_2\text{O}_7^{2-}$ carrier.

Table 3.4-6 : Percentage activities of Cr(VI), M and DP for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ dissolved in 2 ml of 1N H_2SO_4 containing 1g of $\text{Na}_2\text{Cr}_2\text{O}_7$ as a function of the time-interval t.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	82.57 \pm 0.60	9.75 \pm 0.31	7.68 \pm 0.21
5	82.28 \pm 0.46	10.57 \pm 0.19	7.15 \pm 0.27
20	82.82 \pm 0.51	10.88 \pm 0.35	6.30 \pm 0.16
40	83.05 \pm 0.28	11.49 \pm 0.21	5.46 \pm 0.07
60	83.11 \pm 0.37	11.46 \pm 0.09	5.43 \pm 0.28

Table 3.4-7 : Percentage activities of Cr(VI), M and DP for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ dissolved in 2 ml of 0.01N H_2SO_4 containing 500 mg of potassium chrome alum as a function of the time-interval t.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	79.97 \pm 0.72	8.64 \pm 0.46	11.39 \pm 0.26
5	80.80 \pm 0.34	8.81 \pm 0.16	10.39 \pm 0.18
20	77.39 \pm 0.53	13.92 \pm 0.29	8.69 \pm 0.24
40	83.46 \pm 0.49	9.48 \pm 0.27	7.06 \pm 0.22
60	82.62 \pm 0.23	10.59 \pm 0.08	6.79 \pm 0.15

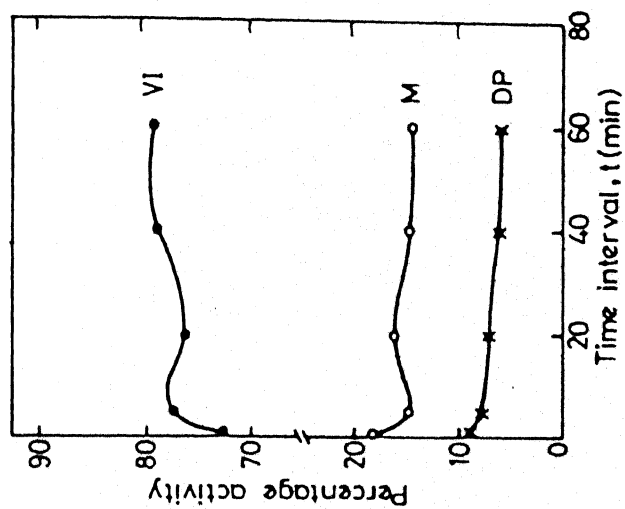


Fig. 3-4-5 Plot of percentage activity vs t for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ in 0.01N H_2SO_4 in presence of excess of Cr^{3+} carrier.

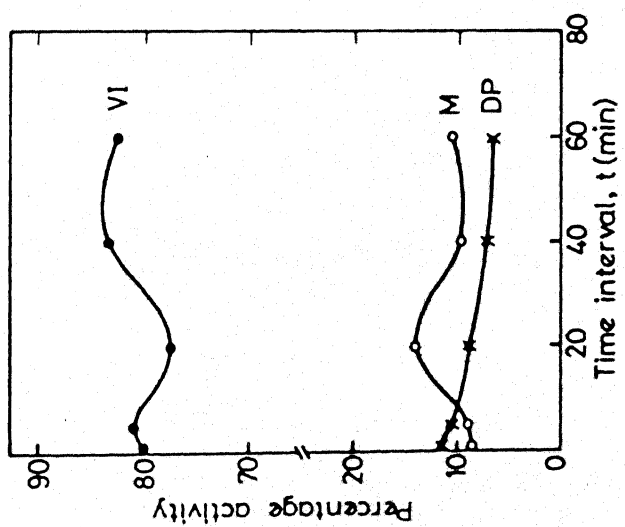


Fig. 3-4-6 Plot of percentage activity vs t for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ in 1N H_2SO_4 in presence of excess of Cr^{3+} carrier.

Table 3.4-8 : Percentage activities of Cr(VI), M and DP for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ dissolved in 2 ml of 1N H_2SO_4 containing 500 mg of potassium chrome alum as a function of the time-interval t.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	72.59 \pm 0.48	18.37 \pm 0.23	9.04 \pm 0.25
5	77.36 \pm 0.49	14.79 \pm 0.26	7.85 \pm 0.23
20	76.27 \pm 0.52	16.38 \pm 0.35	7.35 \pm 0.16
40	78.94 \pm 0.31	14.74 \pm 0.12	6.32 \pm 0.19
60	79.49 \pm 0.26	14.41 \pm 0.08	6.10 \pm 0.18

Table 3.4-9 : Percentage activities of Cr(VI), M and DP for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ dissolved in 2 ml of 1N H_2SO_4 containing 1g of $\text{Na}_2\text{Cr}_2\text{O}_7$ and 500 mg of potassium chrome alum as a function of the time-interval t.

t (min)	Cr (VI) (%)	M (%)	DP (%)
1	82.29 \pm 0.43	8.56 \pm 0.28	9.15 \pm 0.15
5	82.87 \pm 0.51	8.53 \pm 0.27	8.60 \pm 0.24
20	82.98 \pm 0.39	9.41 \pm 0.16	7.61 \pm 0.23
40	83.25 \pm 0.19	9.89 \pm 0.06	6.86 \pm 0.13
60	83.51 \pm 0.36	10.12 \pm 0.21	6.37 \pm 0.15

3.5 Results of the Experiments with TNI Chromium Nitrate

This section presents the results of the experiments with TNI chromium nitrate. The activity which was not retained by either cation or anion exchange column is referred to as a "neutral" ^{51}Cr -species. Conventionally, the eluted cation and the resin held cationic ^{51}Cr -species are designated as M and DP. In all the experiments, using TNI chromium nitrate, a certain amount of activity was found to be held in the anion exchange resin. In the tables below, this species is designated as "resin held anion". In none of the experiments, the presence of $^{51}\text{CrO}_4^{2-}$ or $^{51}\text{Cr}_2\text{O}_7^{2-}$ (i.e., any known form of Cr^{6+} -species) could be detected since no ^{51}Cr -activity could be eluted out from the anion exchange column using the appropriate eluent(s) for chromate or dichromate.

In this section, all data are the results of single measurements.

Table 3.5-1 : Percentage activities of neutral, M, DP and resin held anion for TNI chromium nitrate dissolved in distilled water.

t (min)	Neutral (%)	M (%)	DP (%)	Resin held anion (%)
2	35.90	24.76	8.81	30.53
20	26.43	37.19	8.29	28.09

Table 3.5-2 : Percentage activities of neutral, M, DP and resin held anion for TNI chromium nitrate dissolved in 1N H_2SO_4 at $t = 2$ minutes.

Neutral (%)	M(%)	DP(%)	Resin held anion (%)
26.45	41.43	14.97	17.15

Table 3.5-3 : Counts per minute and percentage activities* of neutral, M, DP and resin held anion for TNI chromium nitrate dissolved in an alkaline medium containing $^{51}\text{CrO}_4^{2-}$ at $t = 2$ minutes.

(Activity of $^{51}\text{CrO}_4^{2-}$ solution before dissolving TNI chromium nitrate = 14446 cpm)

	Neutral	M	DP	Eluted anion ($^{51}\text{CrO}_4^{2-}$)	Resin held anion
cpm	12676	68577	112905	14318	7783
(%)	6.27	33.96	55.92	-	3.85

* All the percentage yields were calculated on the basis of a total excluding the activity due to eluted anion $^{51}\text{CrO}_4^{2-}$.

Table 3.5-4 : Percentage activities of neutral, M, DP and resin held anion for TNI chromium nitrate dissolved in 2 ml of 1N H_2SO_4 containing 10 mg of Na_2CrO_4 as a function of the time-interval t.

t (min)	Neutral (%)	M (%)	DP (%)	Resin held anion (%)
1.5	36.23	43.64	3.23	16.90
15	28.32	62.94	3.93	4.81
180	17.88	70.94	5.05	6.13

Table 3.5-5 : Percentage activities of neutral, M, DP, and resin held anion for TNI chromium nitrate dissolved in 2 ml of 1N H_2SO_4 containing 1g of Na_2CrO_4 as a function of the time-interval t.

t (min)	Neutral (%)	M (%)	DP (%)	Resin held anion (%)
1.5	3.02	63.75	31.05	2.18
15	3.33	69.57	25.43	1.67
30	2.00	73.81	22.40	1.79
60	1.55	79.12	18.35	0.98

Table 3.5-6 : Percentage activities of neutral, M, DP and resin held anion for TNI $\text{Cr}(\text{NO}_3)_3$ dissolved in 2 ml of 1N H_2SO_4 , to which TNI K_2CrO_4 was added after 2 minutes.

For each analysis, volume of aliquot used = 0.15 ml.

Activity of 0.15 ml of TNI chromium nitrate before addition of TNI K_2CrO_4 = 89111 cpm.

Activity of 0.15 ml. of the solution after adding TNI K_2CrO_4 = 145930 cpm.

By subtraction, activity due to TNI K_2CrO_4 = 56819 cpm.

Therefore, in the mixture, 61.06% of TNI $\text{Cr}(\text{NO}_3)_3$ and 38.94% of TNI K_2CrO_4 were present.

t (min)	Neutral (%)	M (%)	DP (%)	Cr (VI) (%)	Resin held anion
2	23.57	28.86	8.33	31.11	8.12
10	21.08	36.49	7.90	28.01	6.50

Significance of all these results will be discussed in Chapter IV.

CHAPTER IV

DISCUSSION

4.1 Trends Observed in Different Types of Experiments

4.1-1 Effect of the Medium of Dissolution on the Time-Variation of ^{51}Cr -Distribution for TNI Chromates and Dichromates

(a) Distilled water without added carrier

The results of the experiments using distilled water alone as the medium of dissolution are shown in Tables 3.1-1, 3.1-2, 3.2-1, 3.3-1 and 3.4-1. The initial yields of Cr^{6+} for all samples are the maximum in this medium compared to any other. For both the potassium salts the initial yields of M and DP are equal, whereas for the sodium salts, DP-yield is less than M-yield.

(b) 0.01N H_2SO_4

From Tables 3.1-3, 3.2-2, 3.3-3 and 3.4-4, it can be seen that the initial yields of Cr^{6+} are always less than those obtained in pure distilled water. Correspondingly, there is an increase in the total amount of Cr^{3+} (M and DP).

This indicates that H_3O^+ ion plays some role in the reduction of Cr^{6+} into Cr^{3+} . It is possible that significant amount of H_2O_2 is generated when a TNI sample, containing

trapped electrons in the crystals, is dissolved in aqueous solution^(16,17). In acid medium, the Cr^{6+} -species would be in the form of dichromate. H_2O_2 , in acidic medium, is known^(56,67) to convert dichromate into perchromic acid which ends up as Cr^{3+} . Thus, H_2O_2 effectively acts as a reducing agent towards dichromate ion.

As regards the time-variation, in the case of TNI K_2CrO_4 , the Cr^{6+} -yield decreases slowly upto about first 30 minutes and then becomes constant. The DP-yield decreases monotonically with time while the M-yield increases (Fig. 3.1-2) with decreasing slope.

For TNI Na_2CrO_4 , there is hardly any change in the yield of any of the species in solution (Fig. 3.2-1).

For TNI $\text{Na}_2\text{Cr}_2\text{O}_7$, the time-variation of the Cr^{6+} -yield is oscillatory in nature and a faint similarity is seen in the case of TNI $\text{K}_2\text{Cr}_2\text{O}_7$. In both the cases, the DP-yield decreases slowly, while the M-yield, corresponding to that of Cr^{6+} -yield, shows an oscillatory nature. There is a net, although small, increase in the Cr^{6+} -yield in about 60 minutes (Figures 3.3-2 and 3.3-4), but the oscillatory change continues even at the end of this time period.

(c) 1N H_2SO_4 : Distinction between the results in 0.01N H_2SO_4 and 1N H_2SO_4 without added carriers

From Tables 3.1-3, 3.1-4, 3.2-2 and 3.2-3, it is seen that the initial yields of Cr^{6+} for both TNI K_2CrO_4

and Na_2CrO_4 increases as one goes from 0.01N H_2SO_4 to 1N H_2SO_4 . It is 5% in the former case and about 1% in the latter.

The nature of the time-variation is similar for TNI chromates in both 0.01N H_2SO_4 and 1N H_2SO_4 (Figures 3.1-2, 3.1-3, 3.2-1 and 3.2-2).

Tables 3.3-4 and 3.4-3 show that the trends in the changes in the initial yields of ^{51}Cr -species are reversed in the case of TNI dichromates. Time-variations in these cases are similar in both 0.01N H_2SO_4 and 1N H_2SO_4 (Figures 3.3-2, 3.3-3, 3.4-2 and 3.4-3).

(d) Effect of the presence of milligram quantities of Cr^{6+} -carrier on the time-variation

Since the TNI samples consisted of milligram quantities of Cr^{6+} -compounds, the solutions used for the experiments automatically contained milligram quantities of Cr^{6+} -carrier. It is clear from all the results shown in Figures 3.1-2, 3.1-3, 3.1-5, 3.3-1 - 3.3-4, 3.3-6, 3.3-8, 3.4-2, 3.4-3, 3.4-5 and 3.4-6, that the presence of milligram quantities of Cr^{6+} -carrier fails to prevent the time-variation of $^{51}\text{Cr}^{6+}$ -yield in solution. This indicates that small quantities of a carrier are unable to prevent the conversion of that particular species into another, and that the effect is probably macroscopic in nature. For TNI K_2CrO_4 , no $^{51}\text{Cr}^{6+}$ -species is generated in solution through any slow reaction since there is a net decrease in its yield. For TNI dichromates the situation is different since the nature of the time-variation of $^{51}\text{Cr}^{6+}$ -species is oscillatory and its

yield at the end of 60 minutes is usually slightly higher than the initial yield.

(e) 1N H_2SO_4 containing Cr^{3+} -carrier

The amount of Cr^{3+} originally present in a sample of TNI chromate or dichromate is extremely small ($\sim 10^{-12}\text{g}$). If macroscopic effects due to the radiation damaged TNI samples are at work, as already mentioned in (d) above, only "large excess" of Cr^{3+} -carrier could prevent the conversion of the initially present $^{51}\text{Cr}^{3+}$ and allow the estimation of the initial distribution of Cr^{3+} .

For TNI K_2CrO_4 and Na_2CrO_4 , although addition of a relatively large amount of Cr^{3+} -carrier (25 mg of Cr^{3+}/ml) causes an overall increase in the total initial yield of Cr^{3+} (M and DP), there is a decrease in the initial yield of monomer (Tables 3.1-6 and 3.2-5) compared to that in the absence of Cr^{3+} -carrier (Tables 3.1-4 and 3.2-3). This increase is by about 5% and 2% for TNI K_2CrO_4 and TNI Na_2CrO_4 respectively.

For TNI K_2CrO_4 , the DP-yield decreases in solution by 8% in the first 30 minutes and then becomes constant. The Cr^{6+} -yield also decreases by about 4% in the first 15 minutes and becomes constant afterwards. Corresponding to these changes, the M-yield increases.

The time-variation of ^{51}Cr -distribution in the case of TNI Na_2CrO_4 is not significant under any condition of dissolution.

Tables 3.3-4 and 3.3-6 show that, for TNI $K_2Cr_2O_7$, there is a decrease in the initial yield of total Cr^{3+} as compared to that in the absence of Cr^{3+} -carrier. The initial M-yield decreases by about 1.5% and DP-yield does not change. Correspondingly, there is an increase in the Cr^{6+} -yield. The nature of the time-variation of Cr^{6+} and M is oscillatory as mentioned earlier in (b).

In the case of TNI $Na_2Cr_2O_7$, Tables 3.4-5 and 3.4-8 show that there is an increase in the initial yield of total Cr^{3+} -species. The M-yield increases by 5.6% whereas the DP-yield decreases by 2%. In solution, the DP-yield decreases slowly at first and then becomes constant. The nature of time-variations of the other two species in solution is again oscillatory.

(f) 1N H_2SO_4 containing excess of Cr^{6+} -carrier

Tables 3.1-5, 3.2-4, 3.3 -5 and 3.4-6 show that in acidic aqueous solutions, the initial yields of Cr^{6+} are maximum in the presence of excess of Cr^{6+} -carrier compared to any other condition and are slightly lower than those in pure water.

From Figures 3.1-4, 3.2-3, 3.3-5 and 3.4-4, it can be seen that the Cr^{6+} -yield does not change with time in solution. Correspondingly, there is no time-variation of the total Cr^{3+} -yield although there is a decrease in the DP-yield and increase in the M-yield.

The amount of Cr^{6+} -species formed at the moment of dissolution is probably "protected" by isotopic dilution with excess of Cr^{6+} which prevents the variation with time. This observation again indicates that a macroscopic effect is at work, as mentioned in (c) above, by which $^{51}\text{Cr}^{6+}$ is reduced in solution through some fast reaction and the process can only be stopped by the addition of an excess of Cr^{6+} -carrier.

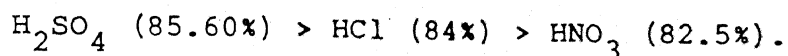
(g) 1N H_2SO_4 containing both Cr^{3+} and Cr^{6+} -carriers in excess

From Tables 3.1-7, 3.2-6, 3.3-7 and 3.4-9, it is seen that, in all the cases, the initial Cr^{6+} -yield under this condition is less than that in the presence of excess of Cr^{6+} -carrier alone, but more than that in the presence of added Cr^{3+} -carrier only. The extent of the change in the initial yield of Cr^{6+} is different in different TNI salts.

There does not seem to be any time-variation of Cr^{6+} -yield. In general, the DP-yield decreases and the M-yield correspondingly increases at first and then the yields of both the species become constant.

(h) Different acids of 0.1N-strength (for TNI $\text{K}_2\text{Cr}_2\text{O}_7$)

Table 3.3-2 shows that the initial yields of Cr^{6+} in TNI $\text{K}_2\text{Cr}_2\text{O}_7$ samples decrease in the following order:



The time-variations of Cr^{6+} - and M-yields in 0.1N HNO_3 (Fig. 3.3-1) and in 0.1N H_2SO_4 (Fig. 3.3-3) are oscillatory in nature but the DP-yield decreases monotonically with time in both the acids.

(j) Effect of the temperature of dissolution in the case of TNI $\text{K}_2\text{Cr}_2\text{O}_7$

From Tables 3.3-8 and 3.3-9, it is seen that the initial yield of Cr^{6+} , and therefore, that of total Cr^{3+} , do not depend on the temperature of dissolution. At 0°C , the initial yields of M and DP are the same whereas at 90°C , the M-yield is higher than the DP-yield. The time-variation of Cr^{6+} -yield is again oscillatory. At 0°C , the DP-yield decreases by about 2% in the first five minutes and then becomes constant, while at 90°C , the DP-yield sharply drops to <1% within 4 minutes. The nature of the time-variation of the M-yield is, as usual, oscillatory although there is an overall increase in its yield probably because DP breaks up into M in solution.

These observations show that (i) the initial yield of Cr^{6+} and the total yield of Cr^{3+} are independent of the temperature of dissolution, (ii) the initial yields of both M and DP are dependent on the dissolution temperature, and (iii) the rate of conversion of DP into M in solution is also temperature dependent.

(k) Non-aqueous solvent - Dimethyl formamide (DMF)

Experiments using DMF as solvent could be carried out only in the case of $\text{TNi} \cdot \text{Na}_2\text{Cr}_2\text{O}_7$ which is soluble in it. Since DMF readily absorbs moisture, dissolution was carried out both in air as well as in nitrogen-atmosphere. From Tables 3.4-2, 3.4-3 and Fig. 3.4-1, the principal observations are:

(i) The initial Cr^{6+} -yield using DMF is more than that using pure distilled water as the solvent and remains constant in solution with time.

(ii) The initial Cr^{6+} -yields are 90% and 86% in DMF in nitrogen-atmosphere and in air, respectively.

(iii) The DP-yield is always higher than the M-yield both in nitrogen-atmosphere and in air.

(iv) The M-yield is lower in nitrogen-atmosphere than in air.

(v) In air, there is a very slow conversion of DP into M with time, but in nitrogen-atmosphere, there is almost no change in DP.

Among aqueous media, the maximum yield of Cr^{6+} obtained (82.7%, Table 3.4-1) is given by pure distilled water. The results of the experiments using DMF show that there might have been much larger amount of Cr^{6+} originally present in the crystal. In aqueous media, partial reduction of Cr^{6+} , possibly by radiolytic processes, produces Cr^{3+} .

This view is also supported by the experiments using DMF in presence of air. Air contains moisture and DMF readily absorbs moisture, which then participates in the reduction of Cr^{6+} into Cr^{3+} .

Higher DP-yield (compared to M-yield) is a possible indication that all or almost all Cr^{3+} is originally present in the DP-form and some M is formed at the instant of dissolution depending on the medium and the temperature of dissolution (Sec. 4.1-1(j)).

Since DMF absorbs moisture rapidly, in the presence of air, small H_2O molecules probably participate in breaking down the DP into M, which may be kinetically controlled. Molecules of DMF are large in size and may not help in breaking some bonds in DP to give M and probably this is the reason why the M-yield using DMF in nitrogen atmosphere is even lower than that in air. In nitrogen atmosphere, the DP-yield does not change with time.

The observed rate of conversion of DP into M has the following dependence on the medium of dissolution:

(DMF in nitrogen atmosphere) < (DMF in presence of air) < (water).

In water this rate increases with increasing temperature. Therefore, two factors are important in the kinetically controlled conversion of DP into M: (i) presence or absence of moisture and (ii) the temperature of dissolution.

(1) Peculiarities in the time-variation curves

The nature of the time-variation of ^{51}Cr -distribution differs from salt to salt. The extent of variation is maximum for K_2CrO_4 and minimum for Na_2CrO_4 .

For TNI K_2CrO_4 , ^{51}Cr -yields vary markedly depending on the presence or absence of added carrier(s). (a) Cr^{6+} -yield decreases as a function of time and reaches a constant value in about 20 minutes. However, in the presence of either excess of Cr^{6+} carrier or excess of both the carriers, there is no time-variation of Cr^{6+} -yields. (b) M-yield increases at a fast rate in the beginning and becomes very slow after about 30 minutes. This increase is always at the expense of Cr^{6+} - and DP-yields. (c) DP-yield always decreases with time and the rate depends on the factors like, the amount of carrier(s) and the temperature of dissolution, as discussed earlier.

The nature of the time-variation of ^{51}Cr -distribution is very different for TNI Na_2CrO_4 . The initial yields of different ^{51}Cr -species vary slightly with the condition of dissolution whereas the time-variations of all ^{51}Cr -species are almost independent of the same. The net maximum change in 60 minutes is about $\pm 1\%$. There is a very slow decrease in DP-yield with time and a corresponding increase in M-yield. In contrast with TNI K_2CrO_4 , in this case, there is always a large difference ($\sim 12 - 18\%$) between the initial yields of M and DP under all experimental conditions. Cr^{6+} -yield is maximum in presence

of excess of Cr^{6+} -carrier and minimum in presence of excess of Cr^{3+} -carrier.

In the presence of excess of Cr^{6+} -carrier alone, the following processes may probably be taking place:

- (i) oxidation of Cr^{3+} into Cr^{6+} , or
 - (ii) prevention of reduction of Cr^{6+} into Cr^{3+} ,
- leading to the maximum initial yield of Cr^{6+} as well as the prevention of its time-variation.

On the other hand, in the presence of excess of Cr^{3+} -carrier, the reverse processes might be taking place:

- (i) reduction of Cr^{6+} into Cr^{3+} , or
 - (ii) prevention of oxidation of Cr^{3+} into Cr^{6+} ,
- both of which would give a maximum yield of Cr^{3+} .

TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ and $\text{K}_2\text{Cr}_2\text{O}_7$ show a different trend regarding the time-variation in ^{51}Cr -distribution. The curves for Cr^{6+} and M are oscillatory in nature, though the extent of this behaviour is much more for TNI $\text{Na}_2\text{Cr}_2\text{O}_7$ than for TNI $\text{K}_2\text{Cr}_2\text{O}_7$. DP-yield decreases with time, at a fast rate in the beginning, then becomes almost constant.

4.1-2 Effect of the Medium of Dissolution on the Time-Variation of ^{51}Cr -Distribution for TNI Chromium Nitrate

The following are the observed ^{51}Cr -species when TNI Cr-nitrate is dissolved in an aqueous medium:

- (i) A neutral ^{51}Cr -species which is not retained by either the cation or the anion exchange resin.

(ii) No elutable $^{51}\text{Cr}^{6+}$ -species (i.e., as CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$) is obtained in any experiment.

(iii) Some ^{51}Cr -activity is found to be retained by the anion exchange resin which is not elutable.

(iv) $^{51}\text{Cr}^{3+}$ -species is observed as M and DP as in the case of chromates and dichromates.

(a) Distilled water

From Table 3.5-1, it can be seen that a large percentage of the total activity is initially obtained as neutral ^{51}Cr -species (36%) and its yield decreases with time.

M and DP-yields are initially less than the yield of the neutral species. The M-yield increases with time and the DP-yield remains almost constant.

The resin-retained anionic activity is also very high initially (30.5%) which decreases slowly with time.

(b) 1N H_2SO_4

It can be seen from Table 3.5-2 that the yield of the neutral ^{51}Cr -species is about 10% less in this case than that in pure water at the same time-interval. Resin-retained anionic activity is also less here by about 13% whereas both M- and DP-yields are higher.

The time-variation of ^{51}Cr -distribution was not studied in this case.

(c) In the presence of $^{51}\text{CrO}_4^{2-}$ in alkaline medium

As shown in Table 3.5-3, the amount of the activity added in the form of $^{51}\text{CrO}_4^{2-}$ is recovered as elutable $^{51}\text{Cr}^{6+}$ (i.e. as $^{51}\text{CrO}_4^{2-}$) quantitatively.

The yields of the neutral and the resin-held anionic species are decreased to a large extent, which could probably be due to the presence of a strong alkali.

Total Cr^{3+} -yield is increased correspondingly, although most of this increase is reflected in the DP-yield.

(d) 1N H_2SO_4 in presence of milligram quantity of Cr^{6+} -carrier

Table 3.5-4 shows that again 36% of ^{51}Cr -activity is obtained as the neutral species and this decreases with time.

The yield of the resin-retained anionic species is equal to that when the sample is dissolved in 1N H_2SO_4 without added carriers. This species also decreases with time.

The total Cr^{3+} (M and DP) activity is lower than that in 1N H_2SO_4 alone. The DP-yield is about 3% whereas the M-yield is about 44% and the latter increases with time at the expense of the neutral as well as the resin-held anionic species. The DP-yield remains almost constant with time in solution.

(e) 1N H₂SO₄ in presence of excess of Cr⁶⁺-carrier

Table 3.5-5 shows that in the presence of an excess of Cr⁶⁺-carrier, almost the whole of the neutral species gets converted into Cr³⁺-species. The resin-held anionic activity is also found to be about 2% initially compared to 17% in 1N H₂SO₄. Both these species decrease with time in solution.

The initial yield of DP is about half that of M, and the DP-yield decreases with time in solution corresponding to an increase in the M-yield.

(f) Chromium nitrate dissolved in 1N H₂SO₄ to which TNI K₂CrO₄ was added after 2 minutes

From Fig. 3.1-3, we get the following results for the distribution of ⁵¹Cr-species among Cr(VI), M and DP from TNI K₂CrO₄ dissolved in 1N H₂SO₄.

	Cr(VI) (%)	M (%)	DP (%)
t=2 min	57.5	31.0	11.5
t=10 min	54.5	35.5	10.0
Difference	3.0	4.5	1.5

From Table 3.5-6, it can be seen that, in the mixture of TNI $\text{Cr}(\text{NO}_3)_3$ and TNI K_2CrO_4 , the activity due to TNI K_2CrO_4 is 38.94%. Therefore, the expected activities due to TNI K_2CrO_4 in the form of Cr(VI), M and DP are the following:

	Cr(VI) (%)	M(%)	DP(%)
t=2 min	$\frac{57.5}{100} \times 38.94 = 22.39$	12.07	4.48
t=10 min	21.22	13.82	3.89

From the results of TNI chromates and dichromates, we know that for these salts, Cr(VI) is obtained only in the form of CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$, i.e., elutable Cr(VI)-species. However, in the case of TNI $\text{Cr}(\text{NO}_3)_3$ dissolved in an aqueous medium, no Cr(VI)-species is obtained as CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$, only a fraction of the activity is retained by the anion exchange column.

Therefore, when a mixture of TNI $\text{Cr}(\text{NO}_3)_3$ and TNI K_2CrO_4 is analyzed, all the elutable Cr(VI)-species is expected to originate from TNI K_2CrO_4 alone, and if this is so, the observed Cr(VI)-activity should be 22.39% and 21.22% at 2 and 10 minutes respectively. But actually the values are much higher: 31.11% and 28.01%, or, 8.7% and 6.79% more than the expected values. This excess Cr(VI)-activity must have formed by the oxidation of some of the species in TNI $\text{Cr}(\text{NO}_3)_3$ crystals when dissolved in

presence of TNI K_2CrO_4 . It is possible that TNI K_2CrO_4 contains considerable amounts of highly oxidizing, radiation damaged species which oxidize some of the species coming from TNI $Cr(NO_3)_3$ in solution to Cr^{6+} .

In solution, Cr^{6+} -activity decreases from 31.11 to 28.01%, i.e., by 3.1% in case of the mixture. From Fig. 3.1-3, it can be seen that Cr^{6+} -activity decreases from 57.5% to 54.5% or by 3% in 10 minutes. This equality in the rate of change of Cr^{6+} -species in solution for the mixture and for TNI K_2CrO_4 alone, indicates that although the initial yield of Cr^{6+} depends on the presence of foreign species in the medium of dissolution, its change with time is probably independent of the presence of small amounts of other species.

The yield of M increases and that of DP decreases in solution as in all other cases, but the rates of these changes are not same as those for TNI K_2CrO_4 or TNI $Cr(NO_3)_3$ considered separately.

4.2 Significance and Probable Interpretation of the Results

Table 4.2-1 summarizes the results of the present investigation at the earliest time after dissolution of the TNI salts in different media under controlled conditions. In the case of TNI K_2CrO_4 , which happens to be the most studied chromate salt, the variation of the distribution is

Table 4.2-1 Initial distribution of ^{51}Cr as percentage activities of Cr(VI), M and DP for different TNI salts as a function of the condition of dissolution.

TNI salt	Condition of dissolution	t (min)	Cr(VI) (%)	M (%)	DP (%)
K_2CrO_4	i) Distilled water in air	2	68.89 ± 0.57	16.49 ± 0.21	14.62 ± 0.36
	ii) Distilled water in nitrogen atmosphere	2	53.10	16.50	16.36
	iii) 0.01N H_2SO_4	1	53.20 ± 0.80	32.62 ± 0.62	14.18 ± 0.18
	iv) 1N H_2SO_4	1	58.28 ± 0.45	29.73 ± 0.14	11.99 ± 0.31
	v) 1N H_2SO_4 + excess of Cr^{6+} - carrier	1	67.49 ± 0.37	18.60 ± 0.25	13.91 ± 0.12
	vi) 1N H_2SO_4 + excess of Cr^{3+} - carrier	1	53.64 ± 0.28	22.88 ± 0.21	23.48 ± 0.07
	vii) 1N H_2SO_4 + excess of both Cr^{6+} and Cr^{3+} -carriers	1	62.41 ± 0.35	19.14 ± 0.30	18.45 ± 0.05
Na_2CrO_4	i) Distilled water in air	2	71.46 ± 0.72	23.69 ± 0.23	4.85 ± 0.49
	ii) 0.01N H_2SO_4	1	68.10 ± 0.46	23.80 ± 0.15	8.10 ± 0.31
	iii) 1N H_2SO_4	1	69.05 ± 0.20	24.03 ± 0.12	6.92 ± 0.08
	iv) 1N H_2SO_4 + excess of Cr^{6+} - carrier	1	71.21 ± 0.48	22.65 ± 0.29	6.14 ± 0.19
	v) 1N H_2SO_4 + excess of Cr^{3+} - carrier	1	67.14 ± 0.66	23.25 ± 0.49	9.61 ± 0.17
	vi) 1N H_2SO_4 + excess of both Cr^{6+} and Cr^{3+} -carriers	1	69.48 ± 0.37	22.49 ± 0.26	8.03 ± 0.11

Continued.....

TNI salt	Condition of dissolution	t (min)	Cr(VI) (%)	M (%)	DP (%)
$K_2Cr_2O_7$	i) Distilled water in air	2	89.02 ± 0.79	5.73 ± 0.44	5.25 ± 0.35
	ii) 0.1N HCl	1.5	84.16 ± 0.51	8.86 ± 0.09	6.98 ± 0.42
	iii) 0.1N HNO_3	1.5	82.53 ± 0.44	9.44 ± 0.16	8.03 ± 0.28
	iv) 0.01N H_2SO_4	1	85.65 ± 0.28	7.46 ± 0.21	6.89 ± 0.07
	v) 0.1N H_2SO_4	1	85.64 ± 0.37	7.47 ± 0.21	6.89 ± 0.15
	vi) 1N H_2SO_4	1	82.39 ± 0.33	10.79 ± 0.30	6.83 ± 0.03
	vii) 1N H_2SO_4 + excess of Cr^{6+} - carrier	1	88.78 ± 0.20	6.02 ± 0.19	5.20 ± 0.01
	viii) 1N H_2SO_4 + excess of Cr^{3+} - carrier	1	84.04 ± 0.28	9.38 ± 0.21	6.58 ± 0.07
	ix) 1N H_2SO_4 + excess of both Cr^{6+} and Cr^{3+} -carriers	1	87.15 ± 0.34	6.86 ± 0.22	5.99 ± 0.12
	x) 1N H_2SO_4 at $0^\circ C$	1	86.74	6.75	6.15
	xi) 1N H_2SO_4 at $90^\circ C$	1	86.66	8.51	4.83
$Na_2Cr_2O_7$	i) Distilled water in air	1	82.74 ± 0.75	10.50 ± 0.70	6.76 ± 0.05
	ii) DMF in nitrogen atmosphere	2	90.74	2.17	7.09
	iii) DMF in air	1.5	86.16	5.27	8.54
	iv) 0.01N H_2SO_4	1	80.54 ± 0.51	10.83 ± 0.19	8.63 ± 0.32

Continued

Table 4.2-1 (Continued):

TNI salt	Condition of dissolution	t (min)	Cr(VI) (%)	M (%)	DP (%)
v)	1N H ₂ SO ₄	1	76.18±0.44	12.71±0.23	11.11±0.21
vi)	1N H ₂ SO ₄ + excess of Cr ₆₊ -carrier	1	82.57±0.60	9.75±0.31	7.68±0.29
vii)	1N H ₂ SO ₄ + excess of Cr ₃₊ -carrier	1	72.59±0.48	18.37±0.23	9.04±0.25
viii)	1N H ₂ SO ₄ + excess of both Cr ₆₊ and Cr ₃₊ carriers	1	82.29±0.43	8.56±0.28	9.15±0.15

the maximum. There is a variation of the yield of $^{51}\text{Cr}^{6+}$ from $\sim 53\%$ in $0.01\text{N H}_2\text{SO}_4$ to $\sim 69\%$ in distilled water. These two extreme values, at a total dose of $\sim 10^{16}$ neutrons ($10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ for 12 hours), are close to the range of the corresponding values from the literature^(8a) as shown in Fig. 4.2-1. The conclusions of Green and Maddock⁽¹¹⁾ and Green et al.⁽¹⁹⁾ that there is neither a time-dependence nor carrier-concentration-dependence of the yield of $^{51}\text{Cr}^{6+}$, do not agree with our observations. The reason possibly lies in the analytical methods used in separating the different species. If there is a dynamic situation existing in the solution of a TNI salt then the addition of too many extraneous but necessary reagents may affect the course of the reactions in solution in unspecified ways.

After the development of the ion exchange method, by Ackerhalt et al.⁽³⁸⁾, no studies of a similar nature were carried out using this comparatively neat method of separation. The elution method used in the present work is simpler compared to that of Ackerhalt et al.⁽³⁸⁾ and there is no perceptible ambiguity in the results thus obtained. From our results, it may be concluded that it is apparently not plausible to assume a one to one correspondence between the observed distribution in solution and that in the original crystal. Further, the time dependence shown in Figures 3.1-2 - 3.1-6, 3.3 -1 - 3.3-8, 3.4-2 - 3.4-7, clearly show that a milligram quantity of CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$ ($\sim 5 \text{ mg/ml}$) is unable to protect the $^{51}\text{Cr}^{6+}$ in the solution. On the other hand, gram-quantities

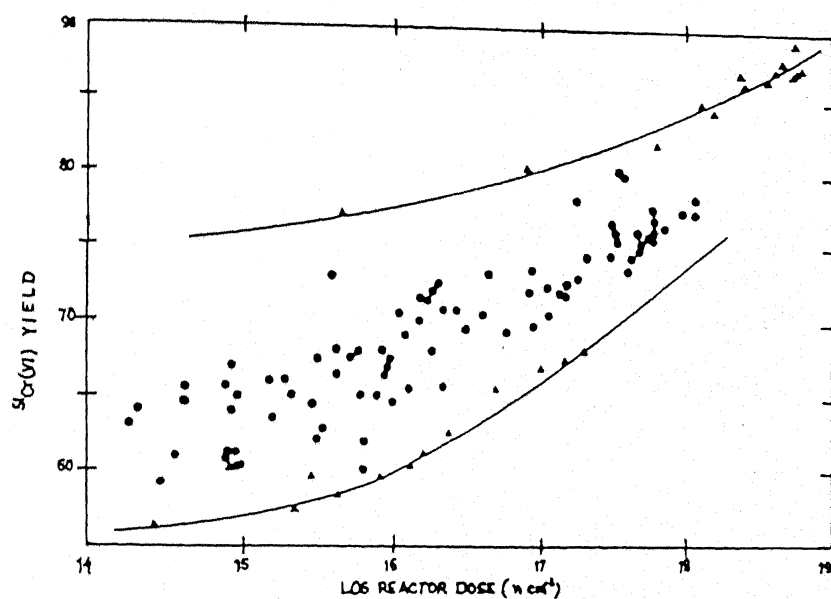


Fig.4.2-1 Literature (8a) values of $^{51}\text{Cr}^{6+}$ -yields for K_2CrO_4 as a function of neutron dose :●-sample irradiated at ambient reactor temperature; upper line - samples irradiated at relatively high reactor temperature; lower line - samples irradiated at ambient reactor temperature and stored, after irradiation, at low temperature.

of $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ protect the $^{51}\text{Cr}^{6+}$ and also give maximum possible yield of $^{51}\text{Cr}^{6+}$. Conversely, excess of Cr^{3+} -carrier gives a maximum initial yield of $^{51}\text{Cr}^{3+}$. Since, time-dependences for $^{51}\text{Cr}^{3+}$ never show any decreasing trend even in the absence of any added Cr^{3+} -carrier, it may be concluded that there is no slow oxidation reaction converting Cr^{3+} into Cr^{6+} . On the other hand, the unmistakable decreasing trend of $^{51}\text{Cr}^{6+}$ -yield in the absence of a large excess of Cr^{6+} -carrier, shows a slow reduction reaction converting $\text{Cr}_2\text{O}_7^{2-}$ into Cr^{3+} , whereas, Fig. 3.1-5 gives an indication of a fast reduction process in presence of excess of Cr^{3+} -carrier. A comparison between Figs. 3.1-3 and 3.1-5 shows almost identical trends. The higher initial yield of DP in one case may be due to the variation in the room temperature with the time gap between the two experiments. Figure 3.3-8 shows how a higher temperature causes a sharp fall in the DP-yield. It is also possible that an excess of Cr^{3+} -carrier does cause a larger yield of DP. Since, the yield of $^{51}\text{Cr}^{6+}$ in both the cases becomes stabilized at $\sim 50\%$, the total Cr^{3+} -yield also becomes constant at $\sim 50\%$ for both. If this reasoning were true then when both Cr^{3+} and Cr^{6+} -carriers are present in excess one should get exactly the same yields as with an excess of Cr^{6+} -carrier alone. Table 4.2-1 shows that the percentage decrease in the yield of Cr^{6+} , as one goes from 1N H_2SO_4 medium containing a large excess of CrO_4^{2-} carrier to

1N H_2SO_4 containing an excess of both Cr^{3+} and CrO_4^{2-} carriers, is practically equal to the corresponding percentage increase in the yield of DP. This is true not only for TNI K_2CrO_4 but also for Na_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$.

Most of the available literature data are on the annealing studies of chromates and dichromates^(68-88,95,98). These data, except the initial retention values (where the salts have been irradiated at ambient reactor temperature), cannot be compared with the results of the present investigation. However, the initial retention values⁽⁸⁾ of TNI Na_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ are in good agreement with our results. This is so, probably because, in these cases the initial yields of Cr^{6+} do not vary significantly with the condition of dissolution and also the time-variation is minimum in these cases. For TNI K_2CrO_4 and $\text{Na}_2\text{Cr}_2\text{O}_7$, the retention values⁽⁸⁾ agree with our results under the conditions where there is no time-variation of $^{51}\text{Cr}^{6+}$ in solution, i.e., when the salt is dissolved in 1N H_2SO_4 containing a large excess of Cr^{6+} -carrier or both Cr^{6+} and Cr^{3+} -carriers in excess.

It has been reported by various authors⁽⁸⁹⁻⁹³⁾ that the e.s.r. spectra of γ -irradiated chromates show the presence of radiation-damaged species, like CrO_4^- , CrO_4^{3-} , CrO_3^- , etc. and Schara et al.⁽⁹⁰⁾ have shown that the e.s.r. spectra of γ -irradiated and neutron-irradiated chromates are similar, indicating that similar species, viz., CrO_4^- , CrO_4^{3-} , CrO_3^- , etc., are also formed in neutron-irradiated chromates. Nothing is known about the kinds of reaction

undergone by these species in solution. The presence and reactions of these species as well as those of hydrated electrons^(16,17) in solution may explain the variation in the ^{51}Cr -distribution in solutions of thermal neutron irradiated chromates and dichromates.

In our experiments with TNI chromium nitrate, the following species were detected after analysis: a neutral ^{51}Cr -species, an anionic species retained by the anion exchange column and $^{51}\text{Cr}^{3+}$ in the form of M and DP. The conclusion drawn by various authors^(23,45,96) that, on bombardment of a Cr(III)-salt, like $\text{Cr}(\text{NO}_3)_3$, with neutron, about 3-10% of Cr^{6+} is obtained when dissolved in aqueous media, does not agree with our results, as we have failed to obtain any Cr^{6+} from TNI $\text{Cr}(\text{NO}_3)_3$. Nothing definite can be said about the neutral ^{51}Cr and the resin-retained anionic activities since the present experimental data are not sufficient for the purpose.

4.3 Proposed Model

No serious attempt has ever been made to explain the observed difference in the retention values obtained using different chromates and dichromates. Also, no mechanism has been proposed as to the formation of $^{51}\text{Cr}^{6+}$ -species in $^{51}\text{Cr}^{3+}$ -doped and $^{51}\text{Cr}^{+}$ -implanted chromates and other salts^(81,84,86,94,97-99). In this work, we have made an attempt to explain the same on the basis of the relative

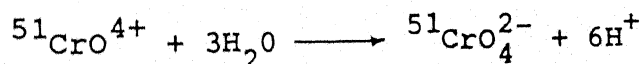
collision probability of a recoil $^{51}\text{Cr}^{6+}$ -species with an O^{2-} ion of the matrix leading to the formation of $^{51}\text{CrO}_4^{4+}$.

4.3.-1 Neutron-Irradiated Chromates and Dichromates

Assumptions

1. Only head-on collisions are effective, which requires the use of the radius of the larger ion instead of the sum of the radii of the two colliding ions in the calculation of the collision cross-section.

2. Because of the high charge states of both $^{51}\text{Cr}^{6+}$ and O^{2-} every such collision between a recoil $^{51}\text{Cr}^{6+}$ ion and an O^{2-} ion will lead to the formation of a $^{51}\text{CrO}_4^{4+}$ ion, which in aqueous solution will hydrolyze giving $^{51}\text{CrO}_4^{2-}$ according to the reaction:



3. $^{51}\text{Cr}^{6+}$ ion after collision with any other ion, like Cr^{6+} or K^+/Na^+ , would retain its identity and in aqueous solution would get converted into $^{51}\text{Cr}^{3+}$.

4. The distance Cr-O has been taken as 1.84 \AA ($= r_{\text{Cr}^{6+}} + r_{\text{O}^{2-}}$) which is somewhat larger than the reported bond distance (d) values⁽¹⁰⁰⁾ [$d_{\text{Cr-O}} = 1.66 \text{ \AA}$ for CrO_4^{2-} , $d_{\text{Cr-O}}$ (terminal) $= 1.63 \text{ \AA}$ and $d_{\text{Cr-O}}$ (bridging) $= 1.79 \text{ \AA}$ for $\text{Cr}_2\text{O}_7^{2-}$], but justifiable on the ground that at the moment the $^{51}\text{Cr}^{6+}$ is recoiling out, the distance may get enlarged because of the loosening of the Cr-O bonds.

On the basis of the above assumptions, we have calculated the relative collision probability between the $^{51}\text{Cr}^{6+}$ and O^{2-} ions in the following manner:

Taking a chromate of general formula M_xCrO_4 , where M^{n+} is a metal ion of charge $n+$ ($x = 1$ for $n = 2$ and $x = 2$ for $n = 1$), the relative probability of formation of CrO^{4+} is given by

$$P = \frac{4 r_{\text{O}^{2-}}^2}{4 r_{\text{O}^{2-}}^2 + x r_{\text{M}^{n+}}^2 + r_{\text{Cr}^{6+}}^2} \quad (4.3-1a)$$

Similarly, for a dichromate $\text{M}_x\text{Cr}_2\text{O}_7$,

$$P = \frac{7 r_{\text{O}^{2-}}^2}{7 r_{\text{O}^{2-}}^2 + x r_{\text{M}^{n+}}^2 + 2 r_{\text{Cr}^{6+}}^2} \quad (4.3-1b)$$

where, r with the appropriate subscript indicates the ionic radius.

The calculated values of P using Equations 4.3-1a and 4.3-1b and the experimental values of $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ yields are presented in Table 4.3-1. Two plots of the percentage yield of $^{51}\text{Cr}^{6+}$ vs. the relative probability P (using two sets of radii values) are shown in Fig. 4.3-1.

Figure 4.3-1 exhibits a linear relation between the yield (Y) of $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ and the relative probability (P) and is given by the equations:

for line I

$$Y = 0.4396 P + 38.25 \quad (4.3-2a)$$

Table 4.3-1 Percentage yields of $^{51}\text{Cr}^{6+}$ and P-values for chromates and dichromates

Compound	$r_{\text{O}^{2-}} = 1.4 \text{ \AA}^{\circ} \#$ $r_{\text{Cr}^{6+}} = 0.44 \text{ \AA}^{\circ} \#$		$r_{\text{O}^{2-}} = 1.32 \text{ \AA}^{\circ} \$$ $r_{\text{Cr}^{6+}} = 0.52 \text{ \AA}^{\circ} \$$		Yield of $^{51}\text{Cr}^{6+}$ (%)
	$r_{\text{M}^{n+}} (\text{ \AA}^{\circ}) \#$	P (%) #	$r_{\text{M}^{n+}} (\text{ \AA}^{\circ}) \$$	P (%) \$	
K_2CrO_4	1.38	66.22	1.33	64.66	67.5*
$\text{K}_2\text{Cr}_2\text{O}_7$	1.38	76.66	1.33	74.92	88.5*
Na_2CrO_4	1.02	77.50	0.97	76.43	71.0*
$\text{Na}_2\text{Cr}_2\text{O}_7$	1.02	84.74	0.97	83.44	82.5* (70.6-80)
PbCrO_4	1.19	82.96	1.02	80.29	73.50
Rb_2CrO_4	1.52	61.98	1.47	59.98	58.1-68.5
SrCrO_4	1.18	83.32	1.12	82.09	72.30
BaCrO_4	1.35	79.59	1.34	77.10	77.20
Cs_2CrO_4	1.67	57.60	1.68	54.37	62.80
ZnCrO_4	0.74	91.38	0.74	89.74	35.00
CaCrO_4	1.00	86.68	0.99	84.74	75.00
MgCrO_4	0.72	97.78	0.66	90.76	53.5-55.8
Li_2CrO_4	0.76	85.31	0.68	85.31	66-83
$\text{Li}_2\text{Cr}_2\text{O}_7$	0.76	89.85	0.68	89.24	54.5
$(\text{NH}_4)_2\text{CrO}_4$	1.42	65.01	1.43	61.85	17.0
$\text{K}_3\text{Cr}_3\text{O}_{10}$	1.38	75.71	1.33	74.00	69-73
CrO_3	-	96.87	-	95.09	65-87

* Results of the present investigation.

All other results are from the literature⁽⁸⁾.

The radii values are from reference - (100).

\$ The radii values are from reference - (101).

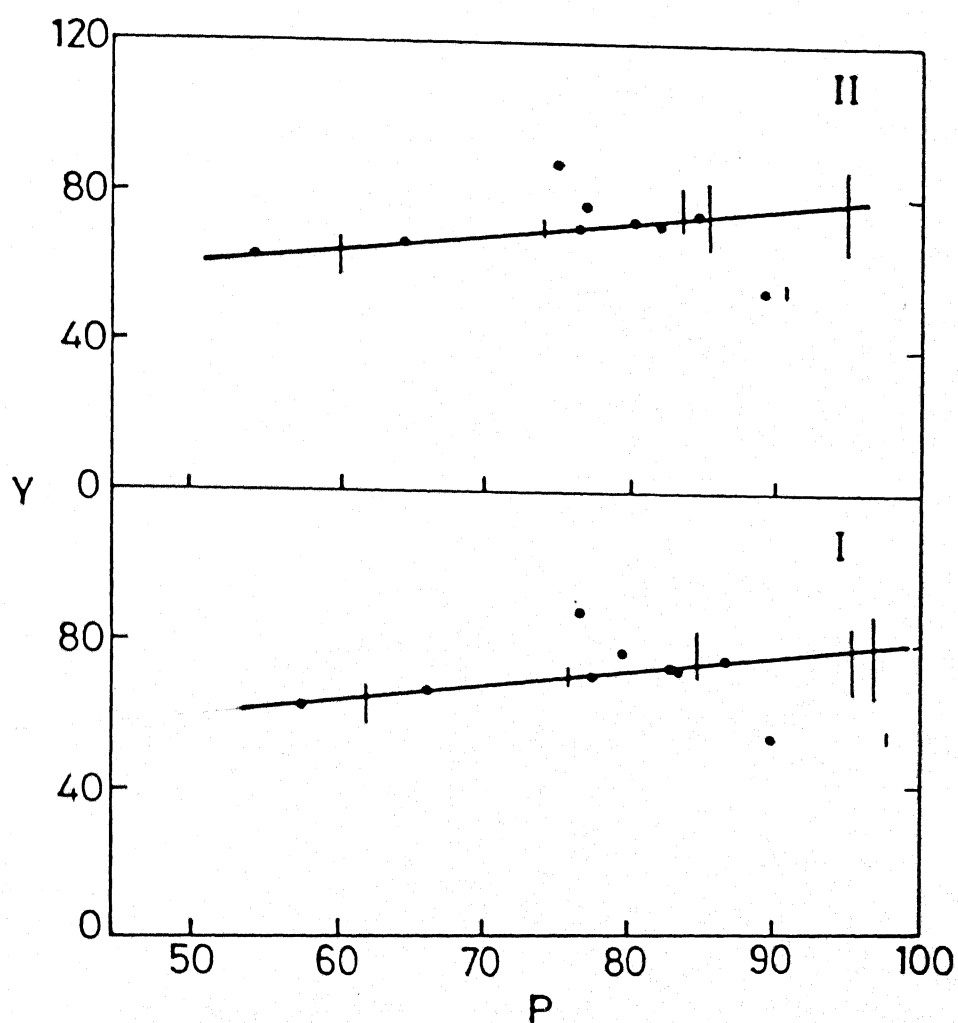


Fig.4.3-1 Plot of percentage yield of $^{51}\text{CrO}_4^{2-}$ Y vs. the calculated probability of collision P,

I. using radii values from reference (100) and

II. using radii values from reference (101).

and for line II,

$$Y = 0.4466 P + 38.33 \quad (4.3-2b)$$

From the two equations 4.3-2a and 4.3-2b, it is obvious that the relative collision probabilities are not very sensitive to small changes in the values of the ionic radii.

Except for $K_2Cr_2O_7$, which gives very high value, and the four salts - $Li_2Cr_2O_7$, $MgCrO_4$, $ZnCrO_4$ and $(NH_4)_2CrO_4$, which give abnormally low values of $^{51}Cr^{6+}$ yields, all the other yields of $^{51}Cr^{6+}$ reported in the literature fall on the straight line quite satisfactorily.

4.3-2 Neutron-Irradiated K_2CrO_4 - K_2BeF_4 Mixed Crystal System

The present model can be extended to explain the observed $^{51}CrO_4^{2-}$ yields in K_2CrO_4 - K_2BeF_4 mixed crystal systems. A two-molecule unit of a uniform 1:1 mixture of K_2CrO_4 - K_2BeF_4 crystal is composed of four K^+ , one Cr^{6+} , four O^{2-} , one Be^{2+} and four F^- ions. The yield of $^{51}CrO_4^{2-}$ can directly be obtained from the considerations in sec. 4.3-1 which is equal to the relative probability of collision between a recoil $^{51}Cr^{6+}$ and O^{2-} ions.

$$P = \frac{4 r_{O^{2-}}^2}{4 r_{K^+}^2 + 4 r_{O^{2-}}^2 + r_{Be^{2+}}^2 + r_{Cr^{6+}}^2 + 4 r_{F^-}^2}$$

Since, $r_{\text{Be}^{2+}} (= 0.27 \text{ \AA}) < r_{\text{Cr}^{6+}}$, $r_{\text{Be}^{2+}}$ has to be replaced by $r_{\text{Cr}^{6+}}$ (assumption (2) in sec. 4.3-1).

$$P = \frac{4 r_{\text{O}^{2-}}^2}{4 r_{\text{K}^+}^2 + 4 r_{\text{O}^{2-}}^2 + 2 r_{\text{Cr}^{6+}}^2 + 4 r_{\text{F}^-}^2}$$

With $r_{\text{F}^-} = 1.33 \text{ \AA}$ and all the other values from reference - (100), we get $P = 34.19\%$. But the observed experimental yield of $^{51}\text{CrO}_4^{2-}$ for a 1:1 mixture of $\text{K}_2\text{CrO}_4 - \text{K}_2\text{BeF}_4$ is $\sim 49\%$ (102).

In an extremely dilute solid solution of $\text{K}_2\text{CrO}_4 - \text{K}_2\text{BeF}_4$ (5 mole percent of K_2CrO_4), the yield of $^{51}\text{CrO}_4^{2-}$ is found to be $\sim 30\%$. Since interactions between $^{51}\text{Cr}^{6+}$ and O^{2-} alone lead to the formation of CrO_4^{2-} , the addition of K_2BeF_4 to K_2CrO_4 has the effect of reducing the interaction probability between $^{51}\text{Cr}^{6+}$ and O^{2-} . According to the present model, the yield of $^{51}\text{CrO}_4^{2-}$ in a solution of 5 mole percent of K_2CrO_4 in K_2BeF_4 should have been given by P'' (with $x = 5$) which is about 3.53% (P'' is evaluated in a later section). This shows that the experimentally observed yield of $\sim 30\%$ in so dilute a solution must be due to an interaction between the recoil $^{51}\text{Cr}^{6+}$ and the oxygen atoms in its immediate environment belonging to the same CrO_4^{2-} . Thus, this 30% yield must be due to a "one shot" or single interaction process. Therefore, in addition to the four earlier assumptions, we have to make three further assumptions.

1. The fraction "f" of $^{51}\text{Cr}^{6+}$ interacting with the O^{2-} and K^+ ions belonging to the K_2CrO_4 molecule undergoing nuclear transformation is given by the ratio of the sum of the effective areas of those ions to the total surface area of a sphere which circumscribes the O^{2-} ions with its centre coinciding with the centre of the Cr^{6+} ion. This is shown schematically in Fig. 4.3-2. Since the K^+ ions lie outside the CrO_4^{2-} ion, one of the two K^+ ions is shown as a small sphere touching the outer surface of the sphere representing the CrO_4^{2-} ion. The yield of $^{51}\text{CrO}^{4+}$ and hence, of $^{51}\text{CrO}_4^{2-}$ is given by $(f \cdot P')$, where P' is the relative probability of collision of $^{51}\text{Cr}^{6+}$ with O^{2-} . The value of P' is slightly different from P for pure K_2CrO_4 (Table 4.3-1), since in the case of mixed crystals, a recoiling $^{51}\text{Cr}^{6+}$ does not see any other Cr^{6+} during the primary collision process with its immediate environment.

2. A $^{51}\text{Cr}^{6+}$ which escapes interaction with the ions of its immediate environment has a relative probability P'' of interaction with an O^{2-} ion in the diluted outer environment. The yield of $^{51}\text{CrO}^{4+}$ due to this fraction $(1-f)$ is given by $[P'' \cdot (1-f)]$.

3. The total relative yield of $^{51}\text{CrO}^{4+}$, in percentage, is given by

$$Y = f \cdot P' + (1-f) \cdot P'' \quad (4.3-3)$$

where P' and P'' are expressed as percentage probabilities.

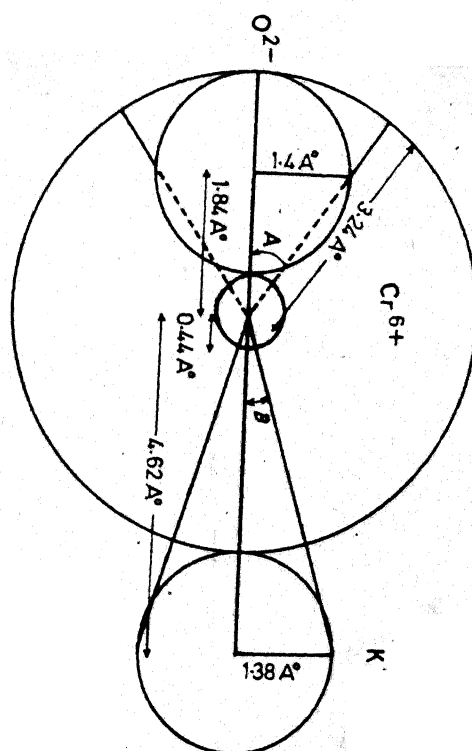


Fig.4.3-2 Schematic representation of the fraction of $^{51}\text{Cr}^{6+}$ escaping from its immediate environment.

Calculation of "f"

In the Fig. 4.3-2, the large circle of radius 3.24 \AA represents the cross-section of the sphere containing Cr^{6+} ion at the centre and four O^{2-} ion tetrahedrally arranged around it and confined within the sphere. The two K^+ ions are touching the outer edge of the large sphere.

The effective areas due to one O^{2-} and one K^+ ions are the areas delineated by the circles of intersection between the respective cones and the large sphere. These two cones have angles $2A$ and $2B$.

From Fig. 4.3-2, these areas can be computed as follows:

$$\text{For one } \text{O}^{2-} \text{ ion, } \hat{A} = \tan^{-1} \frac{1.4}{1.4+0.44} = 37.27^\circ$$

$$\text{and for one } \text{K}^+ \text{ ion, } \hat{B} = \tan^{-1} \frac{1.38}{3.24+1.38} = 16.63^\circ.$$

The surface area of a thin strip of the large sphere lying between the angle θ and $\theta + d\theta$, and ϕ and $\phi + d\phi$, and at a distance R from the origin, is given by

$$R^2 \sin \theta d\theta d\phi.$$

The area of the circular dome of the sphere of radius R lying between the angle 0° and θ is given by,

The rest, i.e., 55% escape into the outer environment and interacts with O^{2-} ions of other K_2CrO_4 molecules.

Calculation of P'

Inside the sphere of radius 3.24 \AA , a recoil $^{51}Cr^{6+}$ cannot collide with any Cr^{6+} ion. It can interact with four O^{2-} and just at the surface of the sphere, with two K^+ ions. Therefore, the relative probability P' of collision between a $^{51}Cr^{6+}$ and four O^{2-} ions in the immediate environment of the recoil $^{51}Cr^{6+}$ is given by

$$P' = \frac{4 r_{O^{2-}}^2}{4 r_{O^{2-}}^2 + 2 r_{K^+}^2} = \frac{7.84}{7.84+3.81} = 0.6729$$

or, in percentage, $P' = 67.29\%$.

Calculation of P''

If x is the mole percent of K_2CrO_4 in the mixed crystal $K_2CrO_4 - K_2BeF_4$, then $(100-x)$ is the mole percent of K_2BeF_4 in the mixture. The probability P'' of interaction of a $^{51}Cr^{6+}$, which escapes into the outer environment, with the O^{2-} of the diluted outer environment is given by,

$$P'' = \frac{\frac{4x}{100} \cdot r_{O^{2-}}^2}{\left[2 \cdot r_{K^+}^2 + \frac{4x}{100} \cdot r_{O^{2-}}^2 + \frac{x}{100} r_{Cr^{6+}}^2 + \frac{(100-x)}{100} \cdot r_{Be^{2+}}^2 + \frac{4(100-x)}{100} \cdot r_{F^-}^2 \right]}$$

Since, $r_{\text{Be}^{2+}} < r_{\text{Cr}^{6+}}$, $r_{\text{Be}^{2+}}$ is replaced by $r_{\text{Cr}^{6+}}$.

$$\therefore P'' = \frac{\frac{4x}{100} \cdot r_{\text{O}^{2-}}^2}{\left[2r_{\text{K}^+}^2 + \frac{4x}{100} \cdot r_{\text{O}^{2-}}^2 + r_{\text{Cr}^{6+}}^2 + \frac{4(100-x)}{100} \cdot r_{\text{F}^-}^2 \right]}$$

Substituting the values of radii from reference - (100),

$$P'' = \left[\frac{7.84x}{11.08 + 0.0076x} \right]$$

Putting the values of f , P' and P'' in Eq. 4.3-3, we get the total probability and hence, the yield of $^{51}\text{CrO}_4^{2-}$ in a mixed crystal of K_2CrO_4 - K_2BeF_4 , as

$$Y = 0.45 \cdot 67.29 + 0.55 \cdot \left[\frac{7.84x}{11.08 + 0.0076x} \right]$$

$$\text{or, } Y = 30.28 + \left[\frac{4.312x}{11.08 + 0.0076x} \right] \quad (4.3-4)$$

The calculated values of Y using Eq. 4.3-4 and those obtained from experiments⁽¹⁰²⁾ for different values of x are shown in Table 4.3-2.

The calculated Y values using Eq. 4.3-4 are in excellent agreement with the experimental values reported by Andersen⁽¹⁰²⁾. The yield of 22.3 - 25% for $x = 1.56$

Table 4.3-2 Calculated values of Y using Eq. 4.3-4 and
the experimental yields of $^{51}\text{CrO}_4^{2-}$ (102)
as a function of x

x	$Y_{\text{calc}} (\%)$	$Y_{\text{lit}} (\%)$
5	32.22	30
25	39.85	40
50	49.09	49
75	58.04	58

mole percent reported by Harbottle⁽²³⁾ does not agree with the calculated value (using Eq. 4.3-4) of 30.89%. According to our model, the minimum possible yield of CrO_4^{2-} must be 30.28%, however small the value of x may be.

CHAPTER V

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

The relative yields of ^{51}Cr as $^{51}\text{Cr}^{3+}$ and $^{51}\text{Cr}^{6+}$ in solutions of thermal-neutron-irradiated chromates and dichromates have been measured. A simple, neat, and efficient, method of separating Cr^{3+} and Cr^{6+} with short-height ion exchange columns has been developed. It has been found that the initial distribution of ^{51}Cr (among its oxidation states) is dependent on the medium of dissolution and on the presence or absence of carrier(s) as well as the amount of the added carrier(s). There is also a variation of ^{51}Cr -distribution in solution with the time gap between dissolution and analysis. An observed reduction of milligram quantities of Cr^{6+} carrier points towards the presence of macroscopic amounts of reducing agents which probably originate in the radiation damage suffered by the crystals.

A correspondence of the right order of magnitude is found to exist between the yield of $^{51}\text{Cr}^{6+}$ in solution and the relative probability of collision between a recoil $^{51}\text{Cr}^{6+}$ and the O^{2-} ions of the CrO_4^{2-} or the $\text{Cr}_2\text{O}_7^{2-}$ ions in the solid state. An extension of this idea leads to the

prediction of the yields of $^{51}\text{Cr}^{6+}$ in thermal-neutron-irradiated $\text{K}_2\text{CrO}_4\text{-K}_2\text{BeF}_4$ mixed crystal systems containing varying amounts of K_2CrO_4 which are in excellent agreement with the corresponding experimental values from the literature.

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